

**Structure elucidation and absolute configuration of metabolites from the soil-derived fungus
Dictyosporium digitatum using spectroscopic and computational methods**

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Supplementary data

Table S1. NMR Spectroscopic Data for **1**

Table S2. NMR Spectroscopic Data for **2**

Table S3. NMR Spectroscopic Data for **3**

Table S4. NMR Spectroscopic Data for **4**

Table S5. NMR Spectroscopic Data for **5**

Table S6. Comparison of Experimental and Calculated ^{13}C and ^1H NMR Chemical Shifts in $\text{DMSO-}d_6$ for (3*R*, 8*R*)-**5** and (3*R*, 8*S*)-**5**

Table S7. NMR Spectroscopic Data for **6**

Table S8. NMR Spectroscopic Data for **7** ($\text{DMSO-}d_6$)

Table S9. NMR Spectroscopic Data for **8** ($\text{DMSO-}d_6$)

Table S10. NMR Spectroscopic Data for **9** ($\text{DMSO-}d_6$)

Table S11. NMR Spectroscopic Data for **10** ($\text{DMSO-}d_6$)

Table S12. NMR Spectroscopic Data for **11** ($\text{DMSO-}d_6$)

Table S13. NMR Spectroscopic Data for **12** ($\text{DMSO-}d_6$)

Table S14. Proton chemical shift differences between (*S*)-MTPA Ester of **1** (**1a**) and (*R*)-MTPA Ester of **1** (**1b**) in $\text{Pyridine-}d_5$

Table S15. Proton chemical shift differences between (*S*)-MTPA Ester of **2** (**2a**) and (*R*)-MTPA Ester of **2** (**2b**) in $\text{Pyridine-}d_5$

Table S16. Proton chemical shift differences between (*S*)-MTPA Ester of **11** (**11a**) and (*R*)-MTPA Ester of **11** (**11b**) in $\text{Pyridine-}d_5$

Table S17. Proton chemical shift differences between (*S*)-MTPA Ester of **12** (**12a**) and (*R*)-MTPA Ester of **12** (**12b**) in $\text{Pyridine-}d_5$

Table S18. Proton chemical shift differences between (*S*)-MTPA Ester of **13** (**13a**) and (*R*)-MTPA Ester of **13** (**13b**) in $\text{Pyridine-}d_5$

Figure S1. ^1H Spectrum of **1** in $\text{DMSO-}d_6$

Figure S2. ^{13}C Spectrum of **1** in $\text{DMSO-}d_6$

Figure S3. HSQC Spectrum of **1** in $\text{DMSO-}d_6$

Figure S4. COSY Spectrum of **1** in $\text{DMSO-}d_6$

Figure S5. HMBC Spectrum of **1** in $\text{DMSO-}d_6$

Figure S6. 1D NOESY Spectra of **1** in $\text{DMSO-}d_6$

Figure S7. ^1H Spectrum of **2** in $\text{DMSO-}d_6$

Figure S8. ^{13}C Spectrum of **2** in $\text{DMSO-}d_6$

Figure S9. HSQC Spectrum of **2** in $\text{DMSO-}d_6$

Figure S10. COSY Spectrum of **2** in $\text{DMSO-}d_6$

Figure S11. HMBC Spectrum of **2** in $\text{DMSO-}d_6$

Figure S12. 2D ROESY Spectra of **2** in $\text{DMSO-}d_6$

Figure S13. ^1H Spectrum of **3** in $\text{DMSO-}d_6$

Figure S14. ^{13}C Spectrum of **3** in $\text{DMSO-}d_6$

Figure S15. HSQC Spectrum of **3** in $\text{DMSO-}d_6$

Figure S16. COSY Spectrum of **3** in $\text{DMSO-}d_6$

Figure S17. HMBC Spectrum of **3** in DMSO-*d*₆
Figure S18. 2D NOESY Spectra of **3** in DMSO-*d*₆
Figure S19. 1D NOESY Spectrum of **3** (irradiated at 4.47ppm) in DMSO-*d*₆
Figure S20. ¹H Spectrum of **4** in DMSO-*d*₆
Figure S21. ¹³C Spectrum of **4** in DMSO-*d*₆
Figure S22. HSQC Spectrum of **4** in DMSO-*d*₆
Figure S23. COSY Spectrum of **4** in DMSO-*d*₆
Figure S24. HMBC Spectrum of **4** in DMSO-*d*₆
Figure S25. 2D ROESY Spectra of **4** in DMSO-*d*₆
Figure S26. 1D NOESY Spectra of **4** in DMSO-*d*₆
Figure S27. ¹H Spectrum of **5** in DMSO-*d*₆
Figure S28. ¹³C Spectrum of **5** in DMSO-*d*₆
Figure S29. HSQC Spectrum of **5** in DMSO-*d*₆
Figure S30. COSY Spectrum of **5** in DMSO-*d*₆
Figure S31. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **5** in DMSO-*d*₆
Figure S32. HMBC ($J_{\text{HC}} = 3$ Hz) Spectrum of **5** in DMSO-*d*₆
Figure S33. ¹H Spectrum of **6** in DMSO-*d*₆
Figure S34. ¹³C Spectrum of **6** in DMSO-*d*₆
Figure S35. HSQC Spectrum of **6** in DMSO-*d*₆
Figure S36. COSY Spectrum of **6** in DMSO-*d*₆
Figure S37. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **6** in DMSO-*d*₆
Figure S38. HMBC ($J_{\text{HC}} = 2$ Hz) Spectrum of **6** in DMSO-*d*₆
Figure S39. 1D NOESY Spectrum of **6** in DMSO-*d*₆
Figure S40. ¹H Spectrum of **7** in DMSO-*d*₆
Figure S41. ¹³C Spectrum of **7** in DMSO-*d*₆
Figure S42. HSQC Spectrum of **7** in DMSO-*d*₆
Figure S43. COSY Spectrum of **7** in DMSO-*d*₆
Figure S44. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **7** in DMSO-*d*₆
Figure S45. HMBC ($J_{\text{HC}} = 3$ Hz) Spectrum of **7** in DMSO-*d*₆
Figure S46. 2D ROESY Spectrum of **7** in DMSO-*d*₆
Figure S47. ¹H Spectrum of **8** in DMSO-*d*₆
Figure S48. ¹³C Spectrum of **8** in DMSO-*d*₆
Figure S49. HSQC Spectrum of **8** in DMSO-*d*₆
Figure S50. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **8** in DMSO-*d*₆
Figure S51. HMBC ($J_{\text{HC}} = 2$ Hz) Spectrum of **8** in DMSO-*d*₆

Figure S52. ^1H Spectrum of **9** in $\text{DMSO-}d_6$
Figure S53. ^{13}C Spectrum of **9** in $\text{DMSO-}d_6$
Figure S54. HSQC Spectrum of **9** in $\text{DMSO-}d_6$
Figure S55. HMBC Spectrum of **9** in $\text{DMSO-}d_6$
Figure S56. ^1H Spectrum of **10** in $\text{DMSO-}d_6$
Figure S57. ^{13}C Spectrum of **10** in $\text{DMSO-}d_6$
Figure S58. HSQC Spectrum of **10** in $\text{DMSO-}d_6$
Figure S59. COSY Spectrum of **10** in $\text{DMSO-}d_6$
Figure S60. HMBC Spectrum of **10** in $\text{DMSO-}d_6$
Figure S61. ^1H Spectrum of **11** in $\text{DMSO-}d_6$
Figure S62. ^{13}C Spectrum of **11** in $\text{DMSO-}d_6$
Figure S63. HSQC Spectrum of **11** in $\text{DMSO-}d_6$
Figure S64. COSY Spectrum of **11** in $\text{DMSO-}d_6$
Figure S65. HMBC Spectrum of **11** in $\text{DMSO-}d_6$
Figure S66. ^1H Spectrum of **12** in $\text{DMSO-}d_6$
Figure S67. HSQC Spectrum of **12** in $\text{DMSO-}d_6$
Figure S68. COSY Spectrum of **12** in $\text{DMSO-}d_6$
Figure S69. HMBC Spectrum of **12** in $\text{DMSO-}d_6$
Figure S70. ^1H Spectrum of (*S*)-MTPA Ester of **1** (**1a**) in $\text{Pyridine-}d_5$
Figure S71. COSY Spectrum of (*S*)-MTPA Ester of **1** (**1a**) in $\text{Pyridine-}d_5$
Figure S72. HSQC Spectrum of (*S*)-MTPA Ester of **1** (**1a**) in $\text{Pyridine-}d_5$
Figure S73. ^1H Spectrum of (*R*)-MTPA Ester of **1** (**1b**) in $\text{Pyridine-}d_5$
Figure S74. COSY Spectrum of (*R*)-MTPA Ester of **1** (**1b**) in $\text{Pyridine-}d_5$
Figure S75. HSQC Spectrum of (*R*)-MTPA Ester of **1** (**1b**) in $\text{Pyridine-}d_5$
Figure S76. ^1H Spectrum of (*S*)-MTPA Ester of **2** (**2a**) in $\text{Pyridine-}d_5$
Figure S77. COSY Spectrum of (*S*)-MTPA Ester of **2** (**2a**) in $\text{Pyridine-}d_5$
Figure S78. HSQC Spectrum of (*S*)-MTPA Ester of **2** (**2a**) in $\text{Pyridine-}d_5$
Figure S79. ^1H Spectrum of (*R*)-MTPA Ester of **2** (**2b**) in $\text{Pyridine-}d_5$
Figure S80. COSY Spectrum of (*R*)-MTPA Ester of **2** (**2b**) in $\text{Pyridine-}d_5$
Figure S81. HSQC Spectrum of (*R*)-MTPA Ester of **2** (**2b**) in $\text{Pyridine-}d_5$
Figure S82. ^1H Spectrum of (*S*)-MTPA Ester of **11** (**11a**) in $\text{Pyridine-}d_5$
Figure S83. COSY Spectrum of (*S*)-MTPA Ester of **11** (**11a**) in $\text{Pyridine-}d_5$
Figure S84. ^1H Spectrum of (*R*)-MTPA Ester of **11** (**11b**) in $\text{Pyridine-}d_5$
Figure S85. COSY Spectrum of (*R*)-MTPA Ester of **11** (**11b**) in $\text{Pyridine-}d_5$
Figure S86. ^1H Spectrum of (*S*)-MTPA Ester of **12** (**12a**) in $\text{Pyridine-}d_5$

Figure S87. COSY Spectrum of (*S*)-MTPA Ester of **12 (12a)** in Pyridine-*d*₅
Figure S88. ¹H Spectrum of (*R*)-MTPA Ester of **12 (12b)** in Pyridine-*d*₅
Figure S89. COSY Spectrum of (*R*)-MTPA Ester of **12 (12b)** in Pyridine-*d*₅
Figure S90. ¹H Spectrum of (*S*)-MTPA Ester of **13 (13a)** in Pyridine-*d*₅
Figure S91. COSY Spectrum of (*S*)-MTPA Ester of **13 (13a)** in Pyridine-*d*₅
Figure S92. ¹H Spectrum of (*R*)-MTPA Ester of **13 (13b)** in Pyridine-*d*₅
Figure S93. ¹H Spectrum of (*R*)-MTPA Ester of **13 (13b)** in Pyridine-*d*₅
Figure S94. Experimental and calculated ECD spectra of **1-3**
Figure S95. ROESY correlations and Mosher's ester analysis of **2**.
Figure S96. COSY, HMBC, and ECD analysis of **5**.
Figure S97. COSY, HMBC, NOESY, and ECD analysis of **6**.
Figure S98. COSY, HMBC, and ECD analysis of **7**.
Figure S99. COSY, HMBC, and ECD analysis of **10**.
Figure S100. COSY, HMBC, and Mosher's ester analysis of **11**.
Figure S101. Mosher's ester analysis of **12** and **13**.

Table S1. NMR Spectroscopic Data for **1** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	NOESY	HMBC
1	40.0	CH ₂	H _α : 1.73, d (17.4) H _β : 1.67, dd (5.4, 17.4)	2	5 9 _β	2, 3, 5, 9, 10 2, 3, 5, 9, 10, 4 _w
2	128.9	CH	5.75, dd (4.8, 10.2)	1 _β , 3	5, 9 _β	1, 4, 10
3	129.7	CH	5.68, d (10.2)	2	5, 9 _β	1, 4, 5, 15
4	81.0	C				
5	45.4	CH	1.92, d (4.8)	6 _β	1 _α , 2, 3, 6 _α , 14, 15 _α , 15 _β , 15- OH	7, 9, 10, 14, 15
6	27.4	CH ₂	H _α : 2.45, d (12.0) H _β : 1.74, dd (4.8, 12.0)		5, 8-OH, 13 _α , 14	4, 5, 8, 10 7, 8, 11
7	86.4	C				
8	69.9	CH	3.61, t (4.8)	9 _β , 8-OH	9 _α , 9 _β , 13 _α , 13	6, 7, 10, 11
9	39.0	CH ₂	H _α : 1.12, d (15.0) H _β : 2.07, dd (5.4, 14.4)		8, 8-OH 1 _β , 2, 3, 8	5, 7, 8, 10, 14 1, 8, 10, 14
10	31.4	C				
11	146.8	C				
12	19.4	CH ₃	1.71, s		8, 8-OH	7, 11, 13
13	111.2	CH ₂	H _α : 4.84, s H _β : 4.76, s		6 _α , 8, 8-OH	7, 11, 12 7, 11, 12
14	28.1	CH ₃	1.15, s		5, 6 _α , 8-OH	1, 5, 9, 10, 2 _w , 4 _w
15	66.6	CH ₂	H _α : 3.23, dd (5.4, 10.2) H _β : 3.13, dd (4.8, 10.2)	15-OH 15-OH	5 5	3, 4, 5 3, 4, 5
8-OH			4.52, d (3.0)	8	6 _α , 9 _α , 13 _α , 12, 14	7, 8, 9
15-OH			4.47, t (6.0)	15	5	4, 15

Table S2. NMR Spectroscopic Data for **2** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	ROESY	HMBC
1	53.9	CH ₂	H _{α} : 2.29, d (14.4) H _{β} : 1.99 (overlap)		3 α , 5, 14 9 β , 14	2, 5, 9, 10, 14, 8 _w 2, 5, 9, 10, 14, 8 _w
2	209.5	C				
3	49.8	CH ₂	H _{α} : 2.44, d (17.4) H _{β} : 2.55, d (17.4)		1 α , 15 15	2, 4, 15 2, 4, 5
4	83.7	C				
5	50.9	CH	2.03, d (4.2)	6 α	1 α , 6 α , 14, 15	1, 7, 9, 10, 14
6	28.5	CH ₂	H _{α} : 2.59, d (12.0) H _{β} : 1.99 (overlap)	5	5, 13 α , 14 13 α , 15	4, 5, 8, 10 4, 5, 8, 10, 11
7	86.4	C				
8	69.6	CH	3.60, t (4.2)	9 β , 8-OH	9 α , 9 β , 12	6, 7, 10
9	40.0	CH ₂	H _{α} : 1.26, d (14.4) H _{β} : 1.53, dd (5.4, 14.4)	8	8, 8-OH 1 β , 3 β , 8	5, 7, 8, 10, 14 1, 8, 10, 14
10	35.3	C				
11	146.9	C				
12	19.4	CH ₃	1.72, s		8, 13 β	7, 11, 13
13	111.1	CH ₂	H _{α} : 4.87, s H _{β} : 4.78, s		6 α , 6 β 12	7, 11, 12 7, 12
14	28.8	CH ₃	1.17, s		1 α , 1 β , 5, 6 α	1, 9, 10, 2 _w
15	30.0	CH ₃	1.18, s		3 α , 3 β , 5, 6 β	3, 4, 5, 2 _w
8-OH			4.75, d (3.6)	8	9 α	7, 8, 9

Table S3. NMR Spectroscopic Data for **3** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	NOESY	HMBC
1	31.0	CH ₂	H _{α} : 1.30 (m) H _{β} : 2.24, td (5.4, 13.8)	2 α , 2 β 2 α , 2 β	2 β , 6 β , 8 β	2, 10, 14
2	37.4	CH ₂	H _{α} : 2.57, td (7.2, 14.4) H _{β} : 2.04, ddd (4.8, 4.8, 14.4)	1 α , 1 β 1 α , 1 β	4, 14 1 α , 1 β	1, 3 1, 3, 4, 10
3	212.3	C				
4	42.4	CH	2.92, p (6.0)	5, 15	2 α , 5, 14	3, 5, 6, 10, 15
5	48.1	CH	1.55, m	4, 6 α , 6 β	4, 13 β , 14, 15	6, 10
6	33.1	CH ₂	H _{α} : 1.83, m H _{β} : 0.81, t (13.8)	5, 15 5	7-OH 1 β , 8 β , 7-OH	5, 7, 8, 10, 11
7	72.2	C				
8	31.4	CH ₂	H _{α} : 1.82, m H _{β} : 1.50, td (13.8, 4.8)	9 α , 9 β 9 α , 9 β	1 β , 6 β , 7-OH	6, 7, 9, 10, 11
9	36.8	CH ₂	H _{α} : 1.29, m H _{β} : 1.33, m	8 α , 8 β 8 α , 8 β	13 β	1, 5, 7, 10, 14 1, 5, 7, 10, 14
10	33.0	C				
11	146.4	C				
12	18.5	CH ₃	1.66, s		13 α , 7-OH	7, 11, 13
13	112.1	CH ₂	H _{α} : 4.92, s H _{β} : 4.85, s		12 5, 9 α	7, 11, 12 7, 11, 12
14	26.9	CH ₃	1.19, s		2 α , 4, 5	1, 5, 9, 10
15	11.4	CH ₃	0.83, d (6.6)	4	5	3, 4, 5
7-OH			4.47, s		6 α , 6 β , 8 β , 12	6, 7, 8, 11

Table S4. NMR Spectroscopic Data for **4** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	NOESY	HMBC
1	38.7	CH	2.69, dt (4.2, 13.2)	2 α , 2 β , 10	2 α , 3 α , 9 α	2, 3, 5, 6, 7, 10, 14
2	26.7	CH ₂	H α : 1.74 (m) H β : 1.48, dq (4.8, 13.2)	1, 3 α 1, 3 α , 3 β	1 3 β , 14	1, 3, 4, 6 1, 3, 6
3	25.0	CH ₂	H α : 2.31, m H β : 2.59, m	2 α , 2 β 2 α	1 2 β	1, 2, 4 1, 2, 4, 5, 15
4	138.0	C				
5	131.5	CH	7.63, s		11	1, 3, 4, 6, 7, 15
6	144.5	C				
7	140.6	C				
8	198.2	C				
9	47.0	CH ₂	H α : 2.24 ^a H β : 2.64, dd (5.4, 16.2)	10	1 14	7, 8 1, 8, 10, 14
10	31.6	CH	2.24 ^a	1, 9 β , 10		8
11	26.0	CH	3.16, p (7.2)	12, 13	5	6, 7, 8, 12, 13
12	20.9	CH ₃	1.13, d (6.6)	11		7, 11, 13
13	21.4	CH ₃	1.17, d (6.6)	11	14	7, 11, 12
14	12.5	CH ₃	0.81, d (6.6)	10	2 β , 9 β , 13	1, 9, 10
15	167.7	C				
15-OH			12.76, br.s			

^a Overlapping signals

Table S5. NMR Spectroscopic Data for **5** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	HMBC
1	168.0	C			
3	110.0	C			
3a	130.1	C			
4	140.6	C			
5	151.2	C			
6	118.0	CH	7.01, d (7.8)	7	1, 4, 7a, 3a _w , 5 _w , 7 _w
7	116.6	CH	7.16, d (7.8)	6	1, 3a, 5, 6, 4 _w
7a	119.5	C			
8	67.3	CH	4.26, q (6.6)	9, 8-OH	3a ^b
9	17.1	CH ₃	1.12, d (6.6)	8	3, 8
3-OCH ₃	50.8	CH ₃	2.97, s		3
4-OH			9.39, s		3a, 4, 5
5-OH			10.51, s		4, 5, 6
8-OH			5.63, br.s	8	^a

^a Not observed^b Observed when HMBC experiment was performed with ⁿ*J*_{CH} = 3 Hz**Table S6.** Comparison of Experimental and Calculated ¹³C and ¹H NMR Chemical Shifts in DMSO-*d*₆ for (3*R*, 8*R*)-**5** and (3*R*, 8*S*)-**5**

Position	δ_C (exp.)	(3 <i>R</i> , 8 <i>R</i>)- 5		(3 <i>R</i> , 8 <i>S</i>)- 5		
		δ_C ^a (calc.)	δ_C ^a (calc.)	δ_H (exp.)	δ_H ^a (calc.)	δ_H ^a (calc.)
1	168.0	168.2	168.7			
3	110.0	108.8	106.6			
3a	130.1	127.3	130.4			
4	140.6	139.0	139.0			
5	151.2	152.7	152.7			
6	117.8	116.7	116.2	7.01	6.94	7.05
7	116.3	119.1	118.4	7.16	7.19	7.32
7a	119.4	118.4	117.3			
8	67.1	74.4	75.7	4.26	4.26	3.93
9	16.9	13.8	15.0	1.12	1.04	1.33
3-OCH ₃	50.6	49.6	48.0	2.97	3.08	2.90
MAE		2.1	2.4		0.06	0.16
DP4		86.5 %	13.5 %		97.00 %	3.00 %

^a Values obtained after systematic errors were removed.

Table S7. NMR Spectroscopic Data for **6** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	NOESY	HMBC
2	153.5	C				
3	102.0	CH	6.27, s			2, 3a, 7a
3a	119.9	C				
4	192.1	C				
5	77.1	CH	3.89, dd (4.8, 7.8)	6, 5-OH	7 β	4, 6, 7
6	70.7	CH	3.95, m	5, 7 α , 7 β , 6-OH	7 α , 7 β	5, 7a
7	30.4	CH ₂	H α : 3.15, dd (4.8, 16.8) H β : 2.80, dd (7.8, 16.8)	6, 7 β 6, 7 α	7 β , 6 7 α , 5, 6	3a, 5, 6, 7a 3a, 5, 6, 7a, 3 ^a
7a	162.4	C				
8	13.1	CH ₃	2.27, s			2, 3, 3a ^a , 7a ^a , 4 ^a
5-OH			5.50, d (4.2)	5		4, 5, 6
6-OH			5.44, d (4.2)	6		5, 6, 7

^a Observed when HMBC experiment was performed with ${}^nJ_{CH} = 2$ Hz

Table S8. NMR Spectroscopic Data for **7** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	ROESY	HMBC
2	158.2	C				
3	108.1	CH	6.39, s		8, 9 α	2, 3a, 7a
3a	143.1	C				
4	36.4	CH	2.91, m	5 α , 5 β , 9 α , 9 β	5 α	5, 3a, 9
5	26.7	CH ₂	H α : 2.10, m H β : 1.82, m	4, 6 4, 6	4	3a, 4, 6, 7, 9, 3 ^a 3a, 4, 6, 7, 9
6	36.2	CH ₂	2.43, m	5 α , 5 β		4, 5, 7, 7a
7	184.2	C				
7a	145.9	C				
8	13.7	CH ₃	2.34, s		3	2, 3, 3a ^a , 7a ^a
9	63.2	CH ₂	H α : 3.64, m H β : 3.52, m	4, 9-OH 4, 9-OH	3	3a, 4, 5 3a, 4, 5
9-OH			4.87, t (5.4)	9		4, 9

^a Observed when HMBC experiment was performed with ${}^nJ_{CH} = 3$ Hz

Table S9. NMR Spectroscopic Data for **8** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	HMBC
2	157.0	C		
3	101.8	CH	6.98, s	2, 3a, 7a
3a	120.2	C		
4	127.7	C		
5	115.3	CH	7.25, s	3a, 6, 7, 9, 3 ^b
6	154.6	C		
7	103.6	CH	7.21, s	3a, 5, 6, 7a
7a	155.7	C		
8	13.8	CH ₃	2.44, s	2, 3, 3a _w
9	192.4	C	10.07, s	3a, 4, 5, 7a _w
6-OH			^a	

^a Not observed^b Observed when HMBC experiment was performed with ⁿ*J*_{CH} = 2 Hz**Table S10.** NMR Spectroscopic Data for **9** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	HMBC
2	157.9	C		
3	103.1	CH	7.05, s	2, 3a, 7a
3a	129.6	C		
4	119.1	C		
5	131.8	CH	7.55, d (8.4)	3a, 7, 9, 3a _w
6	110.4	CH	6.73, d (7.8)	4, 7a, 7 _w
7	150.5	C		
7a	143.5	C		
8	13.8	CH ₃	2.47, s	2, 3, 3a _w
9	189.7	C	9.83, s	3a, 4, 5, 7a _w
7-OH			^a	

^a Not observed

Table S11. NMR Spectroscopic Data for **10** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	HMBC
1	127.4	C			
2	152.8	C			
3	34.6	CH ₂	H _β : 2.82, dd (3.6, 17.4)	4	1, 2, 4, 5
			H _α : 2.50 ^a	4	1, 2, 4, 5
4	64.3	CH	4.09, m	3 α , 3 β , 5 α , 5 β	^a
5	46.1	CH ₂	H _β : 2.60, dd (3.0, 15.6)	4	3, 4, 6
			H _α : 2.39, dd (7.2, 15.6)	4	3, 4, 6
6	196.8	C			
7	55.5	CH ₂	H _α : 4.82, d (11.4)		1, 2, 6, 1'
			H _β : 4.79, d (11.4)		1, 2, 6, 1'
8	128.7	CH	6.68, d (15.0)	9	10
9	137.0	CH	6.44, m	8, 10	2, 10
10	19.2	CH ₃	1.90, d (6.6)	9	8, 9, 2 _w
1'	170.3	C			
2'	20.7	CH ₃	1.96, s		1'
4-OH			^b		

^a Underneath the DMSO signals^b Not observed

Table S12. NMR Spectroscopic Data for **11** (DMSO-*d*₆)

Position	δ_C		δ_H (<i>J</i> in Hz)	COSY	HMBC
1	161.7	C			
2	111.8	CH	6.11, d (9.6)	3	1, 4
3	149	CH	7.40, d (9.0)	2	1, 5, 6
4	113.1	C			
5	159.2	C			
6	36.4	CH ₂	H _{α} : 2.39, dd (4.2, 14.4) H _{β} : 2.28, dd (8.4, 14.4)	6 _{β} , 7 6 _{α} , 7	3, 4, 5, 7, 8 3, 4, 5, 7, 8
7	71.3	CH	3.42, m	6 _{α} , 6 _{β} , 8 _{α} , 8 _{β} , 7-OH	4, 9
8	29.6	CH ₂	H _{α} : 1.42, m H _{β} : 1.33, m	7, 8 _{β} , 9 7, 8 _{α} , 9	6, 7, 9 6, 7, 9
9	10.1	CH ₃	0.89, t (7.2, 7.8)	8 _{α} , 8 _{β}	7, 8
10	17.3	CH ₃	2.19, s		4, 5, 3 _w , 7 _w
7-OH			4.56, d (5.4)	7	6, 7, 8

Table S13. NMR Spectroscopic Data for **12** (DMSO-*d*₆)

Position	δ_C ^a		δ_H (<i>J</i> in Hz)	COSY	HMBC
1	161.6	C			
2	112.1	CH	6.13, d (9.6)	3	1, 4
3	147.8	CH	7.41, d (9.0)	2	1, 5, 6
4	115.1	C			
5	158.3	C			
6	25.0	CH ₂	H _{α} : 2.30, m H _{β} : 2.36, m	7 7	3, 4, 5, 7 3, 4, 5, 7
7	38.8	CH ₂	1.45, q (7.2)	6	^b
8	64.8	CH	3.55, m	7, 9, 8-OH	^b
9	23.6	CH ₃	1.07, d (6.0)	8	7, 8
10	16.8	CH ₃	2.19, s		4, 5
8-OH			4.48, d (4.8)	8	7, 8

^a Determined from HSQC and HMBC spectra^b Not observed

Table S14. Proton chemical shift differences between (*S*)-MTPA Ester of **1 (1a)** and (*R*)-MTPA Ester of **1 (1b)** in Pyridine-*d*₅

Position		δ_{H} (1a)	δ_{H} (1b)	$\Delta\delta^{\text{SR}}$
1	CH ₂	1.65	1.73	-0.08
		1.65	1.73	-0.08
2	CH	5.81	5.83	-0.02
3	CH	6.00	5.96	+0.04
5	CH	1.93	2.02	-0.09
6	CH ₂	2.40	2.41	-0.01
		2.16	2.09	+0.07
8	CH	5.47	5.54	-0.07
9	CH ₂	2.33	2.42	-0.09
		1.33	1.42	-0.09
12	CH ₃	1.94	1.91	+0.03
13	CH ₂	5.04	4.84	+0.20
		5.02	4.77	+0.25
14	CH ₃	0.80	1.11	-0.31
15	CH ₂	4.62	4.61	+0.01
		4.19	4.24	-0.05

Table S15. Proton chemical shift differences between (*S*)-MTPA Ester of **2 (2a)** and (*R*)-MTPA Ester of **2 (2b)** in Pyridine-*d*₅

Position		δ_{H} (2a)	δ_{H} (2b)	$\Delta\delta^{\text{SR}}$
1	CH ₂	2.25	2.32	-0.07
3	CH ₂	2.99	3.01	-0.02
		2.51	2.53	-0.02
5	CH	1.99	2.03	-0.04
6	CH ₂	2.42	2.44	-0.02
		2.25	2.18	+0.07
8	CH	5.39	5.46	-0.07
9	CH ₂	1.98	2.06	-0.08
		1.46	1.55	-0.09
12	CH ₃	1.92	1.90	+0.02
13	CH ₂	5.02	4.84	+0.18
		5.01	4.78	+0.23
14	CH ₃	1.23	1.23	0.00
15	CH ₃	0.85	1.15	-0.30

Table S16. Proton chemical shift differences between (*S*)-MTPA Ester of **11** (**11a**) and (*R*)-MTPA Ester of **11** (**11b**) in Pyridine-*d*₅

Position	δ_{H} (11a)	δ_{H} (11b)	$\Delta\delta_{\text{H}}^{\text{SR}}$
2	6.29	6.18	+0.11
3	7.31	7.18	+0.13
6	2.69	2.58	+0.11
	2.55	2.47	+0.08
7	5.27	5.27	0.00
8	1.64	1.67	-0.03
9	0.84	0.93	-0.09
10	2.09	1.88	+0.21

Table S17. Proton chemical shift differences between (*S*)-MTPA Ester of **12** (**12a**) and (*R*)-MTPA Ester of **12** (**12b**) in Pyridine-*d*₅

Position	δ_{H} (12a)	δ_{H} (12b)	$\Delta\delta^{\text{SR}}$
2	6.28	6.25	+0.03
3	7.16	7.05	+0.11
6	2.30	2.13	+0.17
	2.25	2.12	+0.13
7	1.77	1.68	+0.09
	1.67	1.62	+0.04
8	5.26	5.26	0.00
9	1.28	1.35	-0.07
10	2.04	1.93	+0.11

Table S18. Proton chemical shift differences between (*S*)-MTPA Ester of **13** (**13a**) and (*R*)-MTPA Ester of **13** (**13b**) in Pyridine-*d*₅

Position	δ_{H} (13a)	δ_{H} (13b)	$\Delta\delta^{\text{SR}}$
2	6.43	6.29	+0.14
3	7.54	7.18	+0.36
6	6.00	5.92	+0.08
7	1.61	1.63	-0.02
	1.85	1.87	-0.02
8	1.09	1.26	-0.17
	1.23	1.31	-0.08
9	0.79	0.85	-0.06
10	2.36	2.33	+0.03

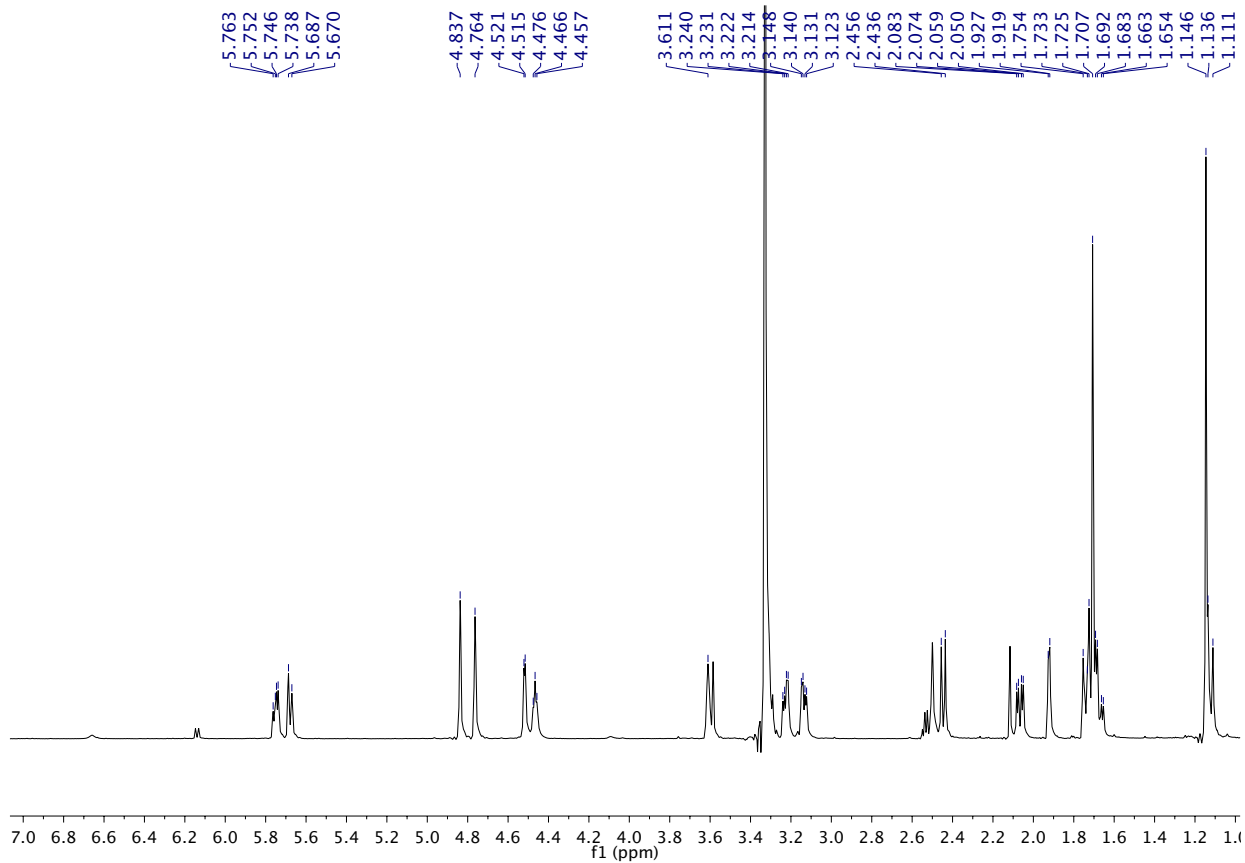


Figure S1. ^1H Spectrum of **1** in $\text{DMSO-}d_6$

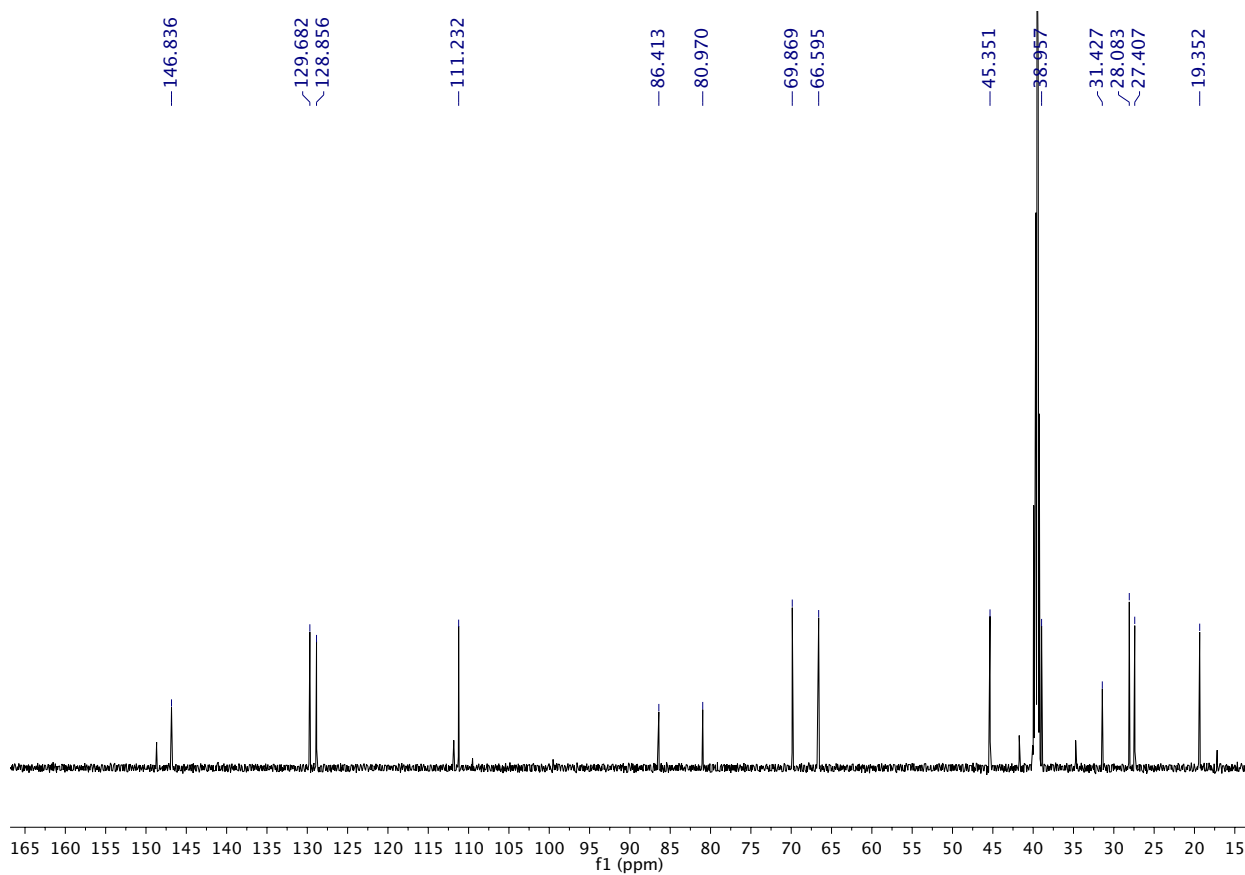


Figure S2. ^{13}C Spectrum of **1** in $\text{DMSO-}d_6$

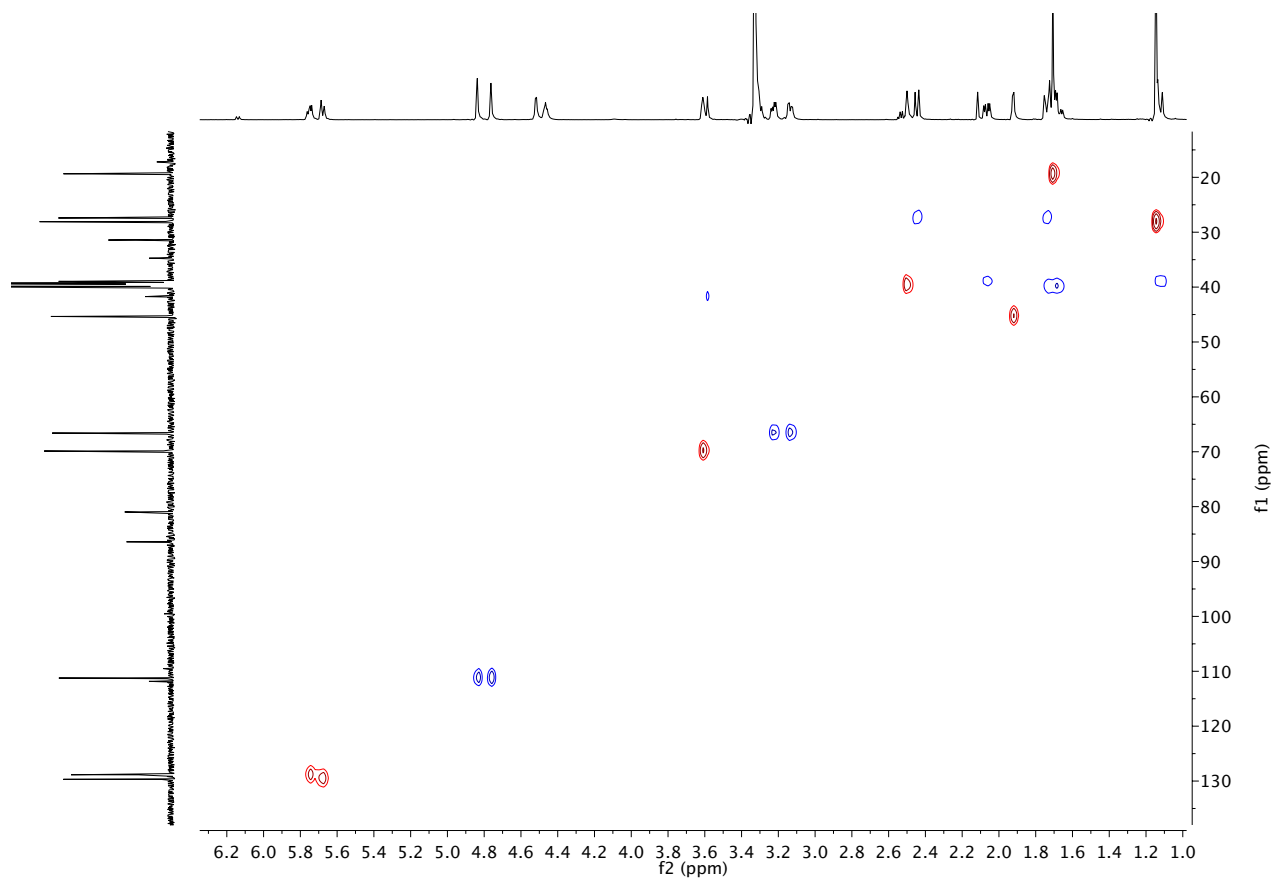


Figure S3. HSQC Spectrum of 1 in DMSO- d_6

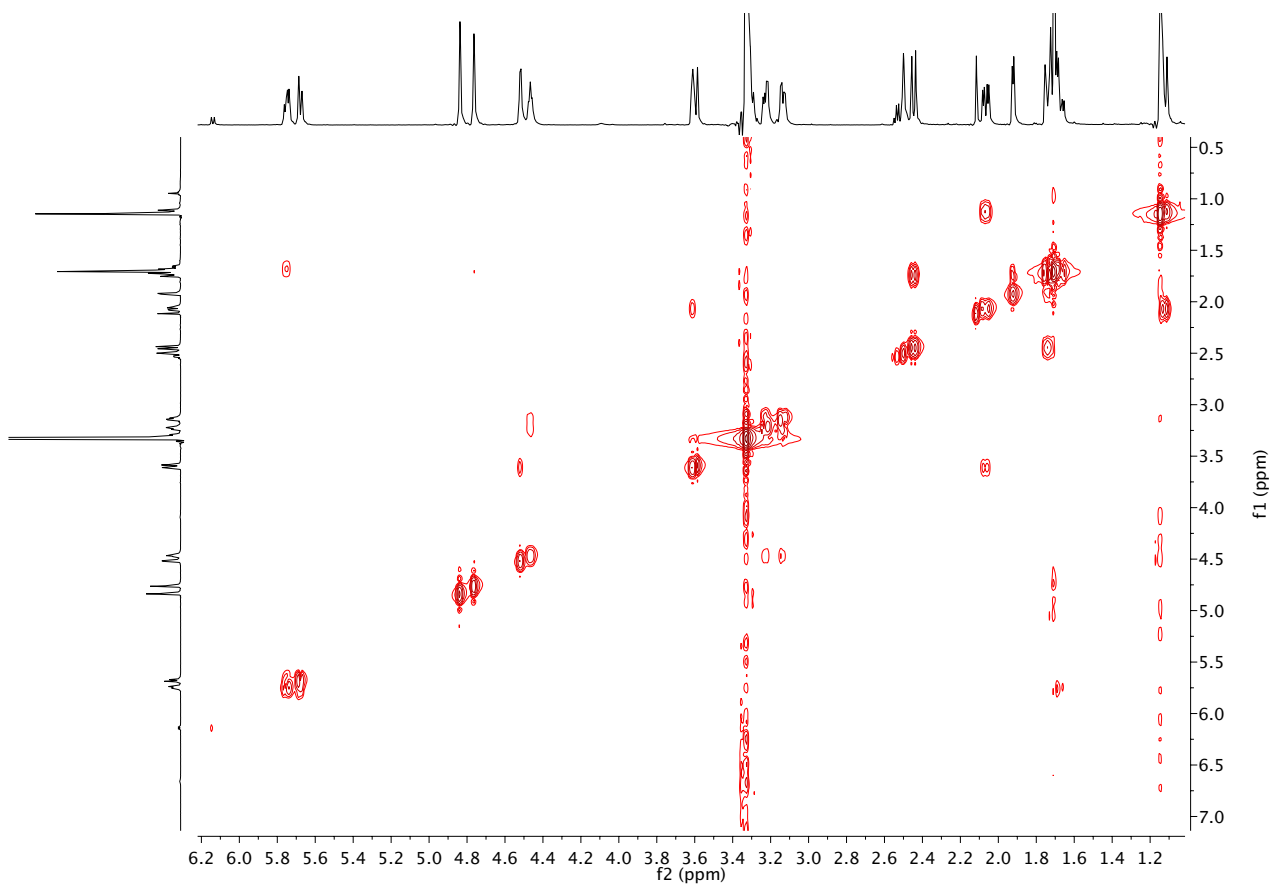


Figure S4. COSY Spectrum of 1 in DMSO- d_6

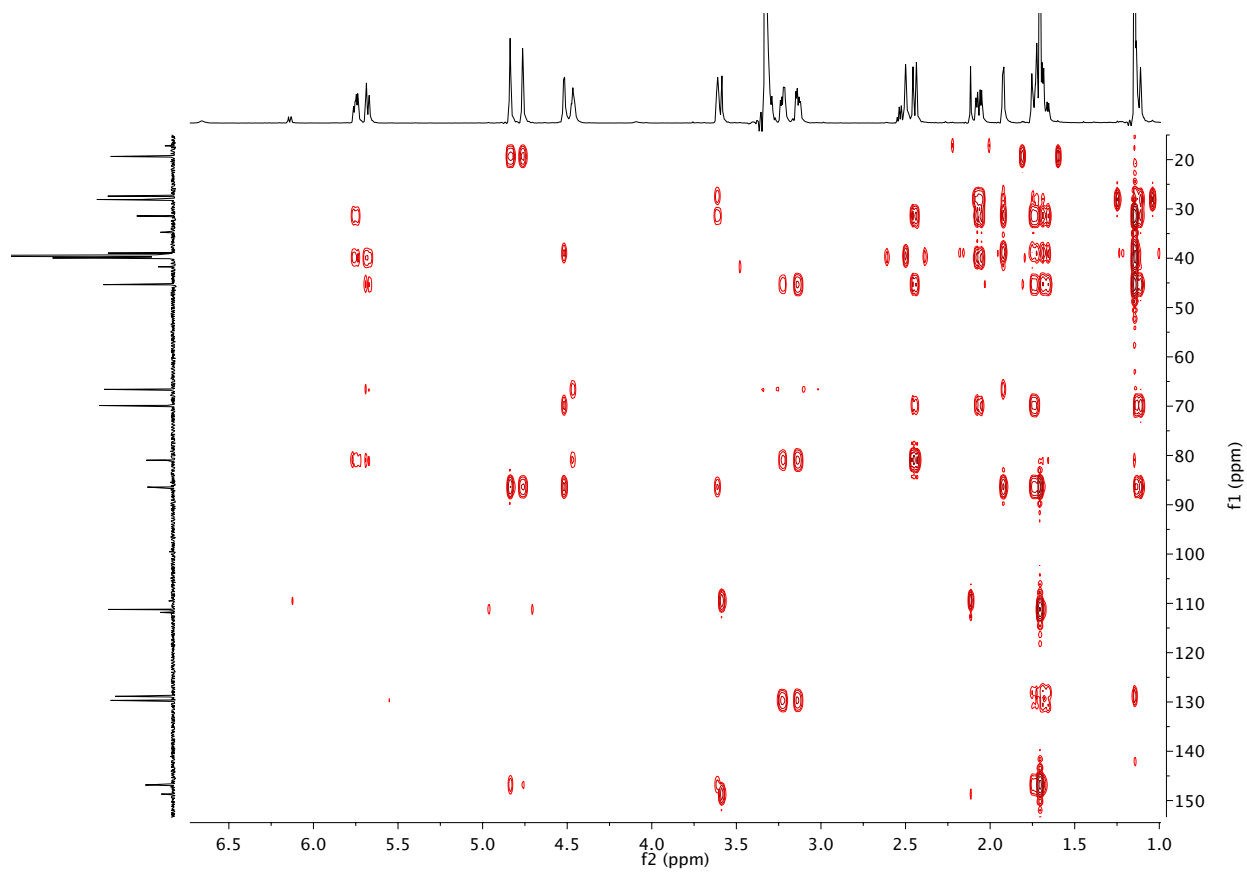


Figure S5. HMBC Spectrum of **1** in DMSO- d_6

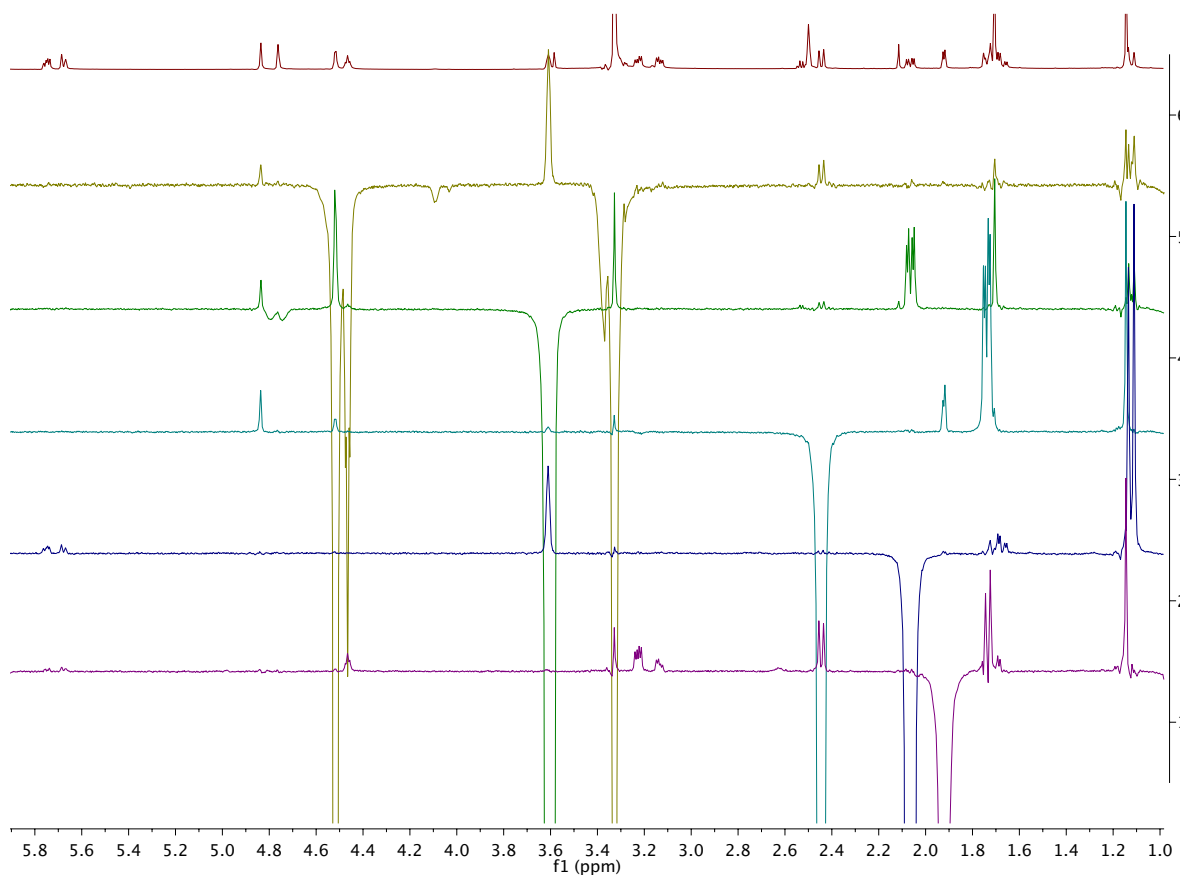


Figure S6. 1D NOESY Spectra of **1** in DMSO- d_6

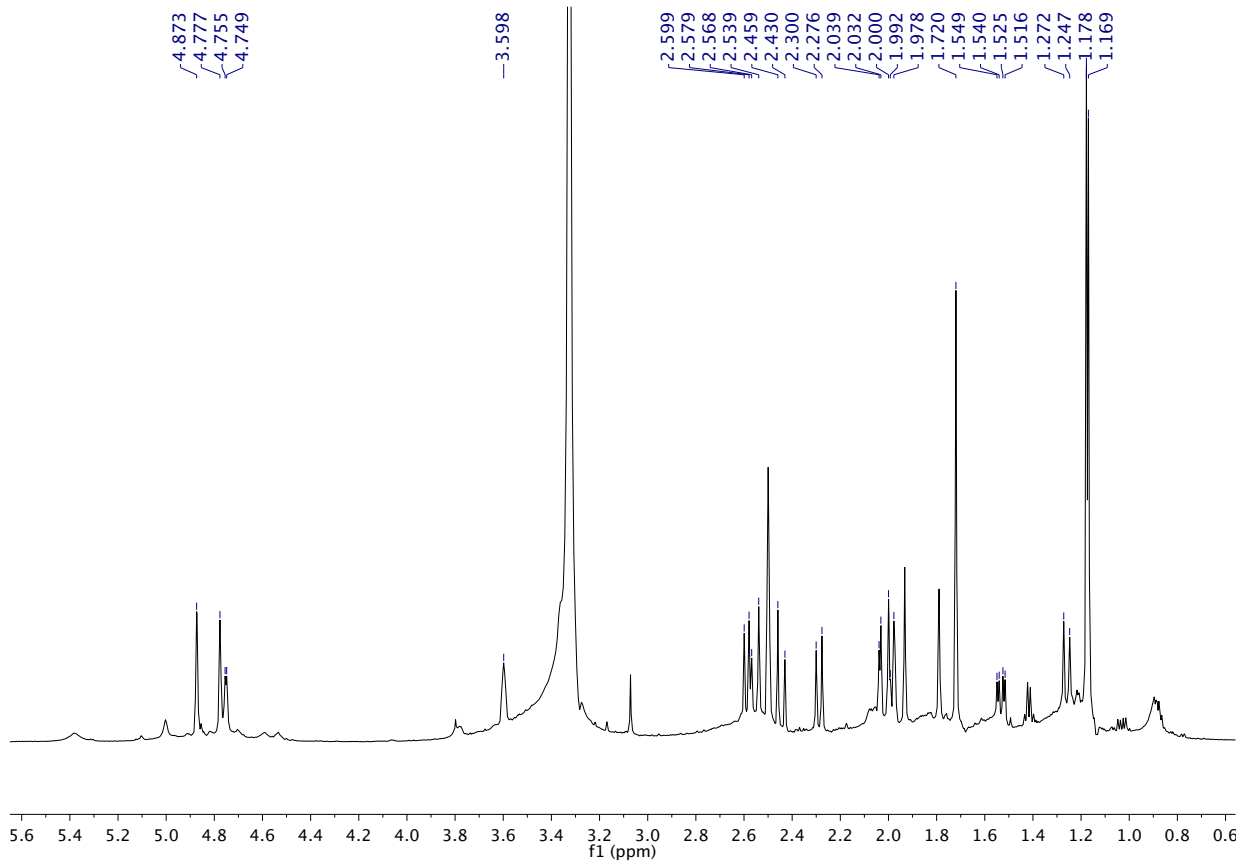


Figure S7. ^1H Spectrum of **2** in $\text{DMSO-}d_6$

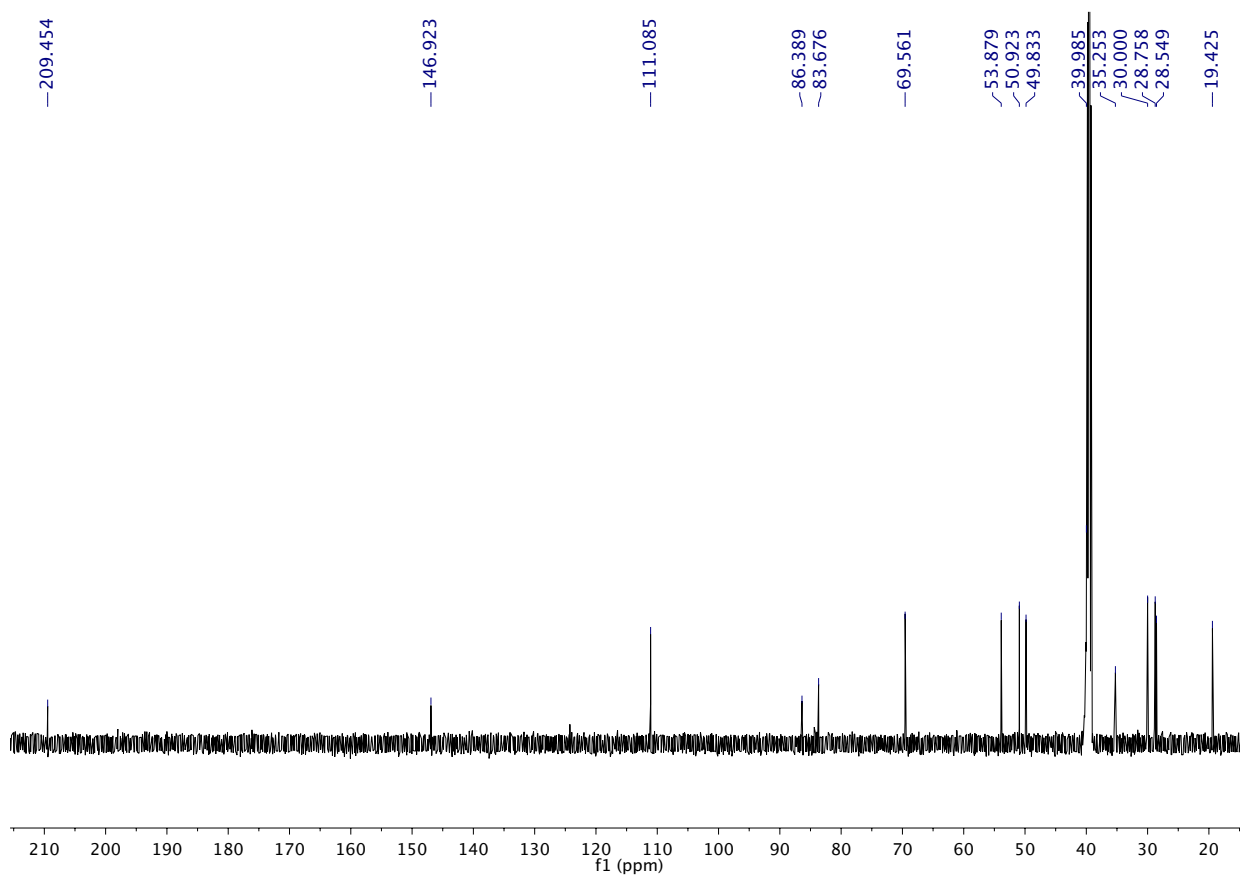


Figure S8. ^{13}C Spectrum of **2** in $\text{DMSO-}d_6$

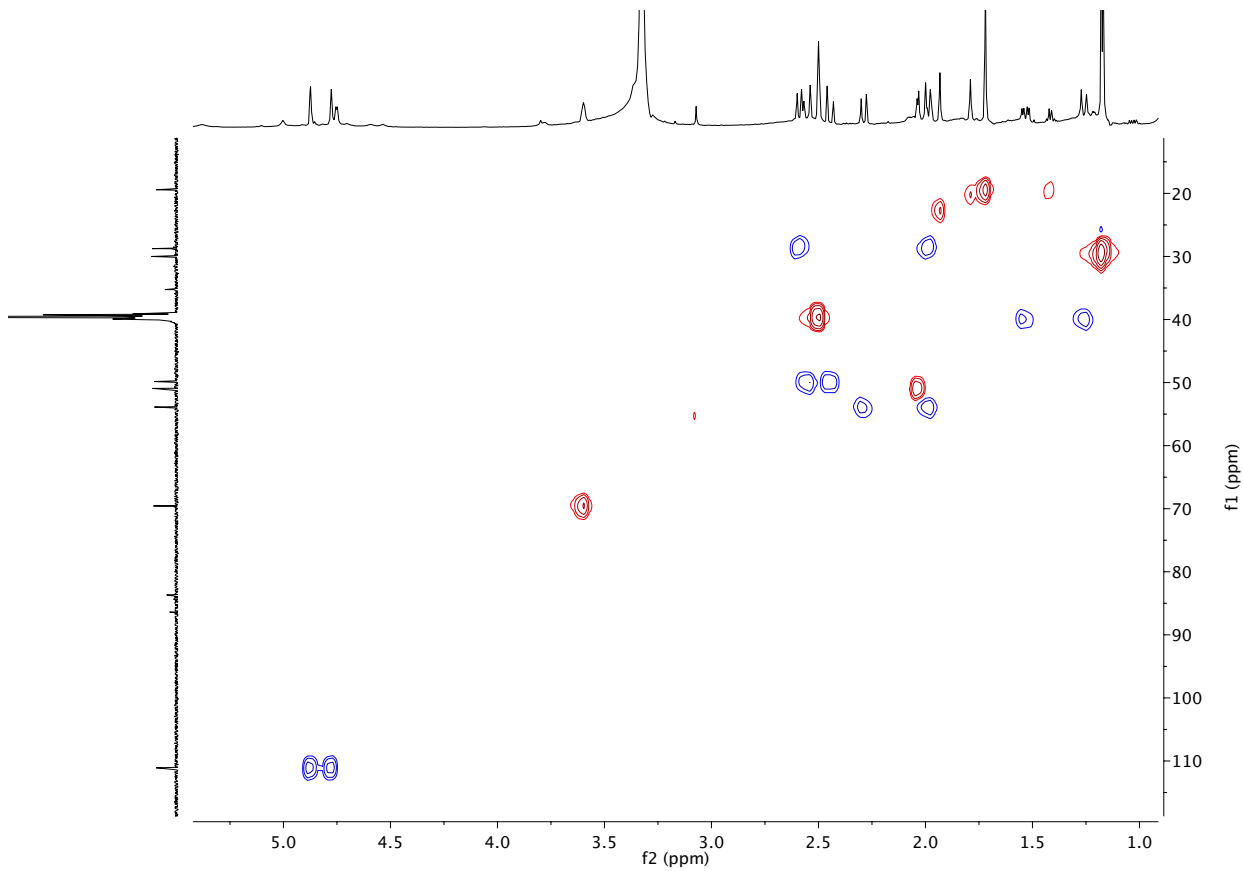


Figure S9. HSQC Spectrum of **2** in DMSO- d_6

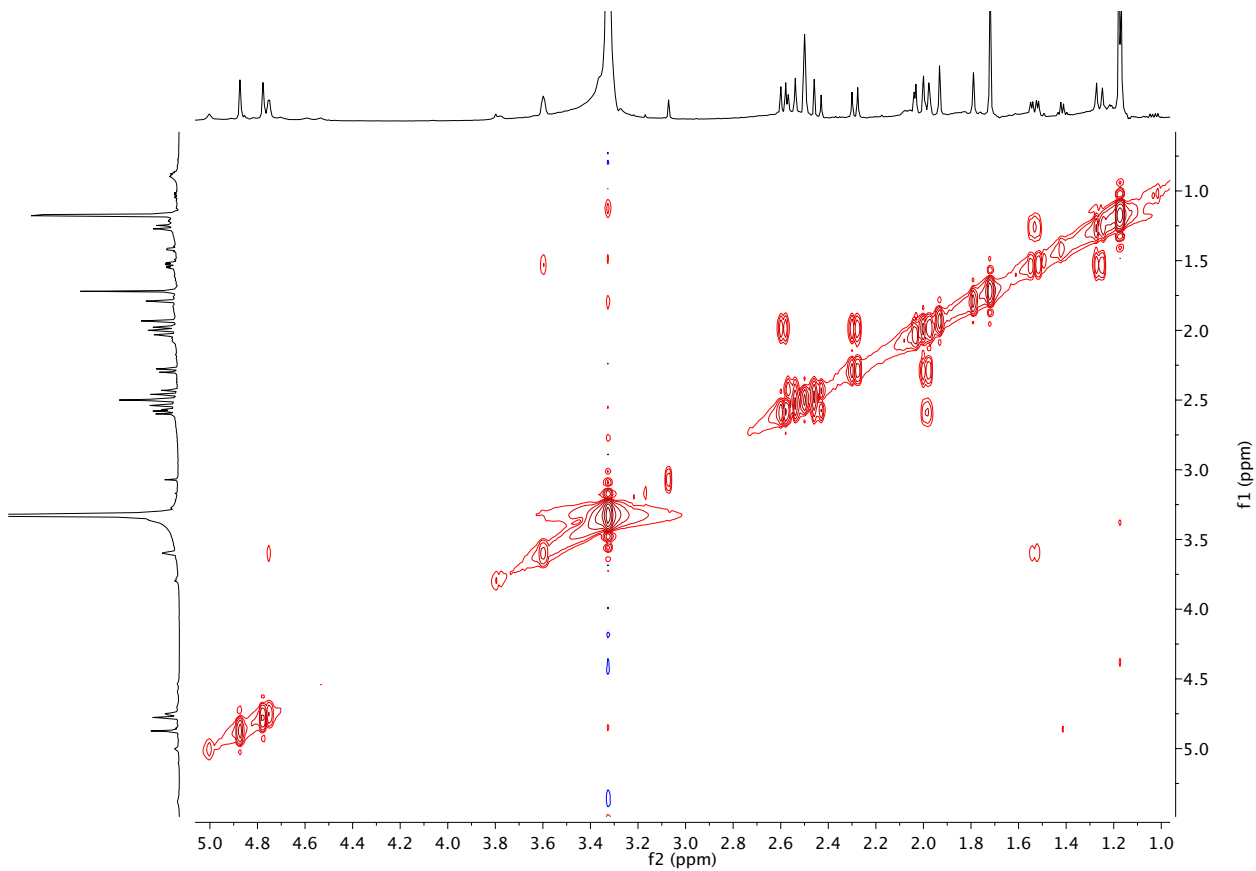


Figure S10. COSY Spectrum of **2** in DMSO- d_6

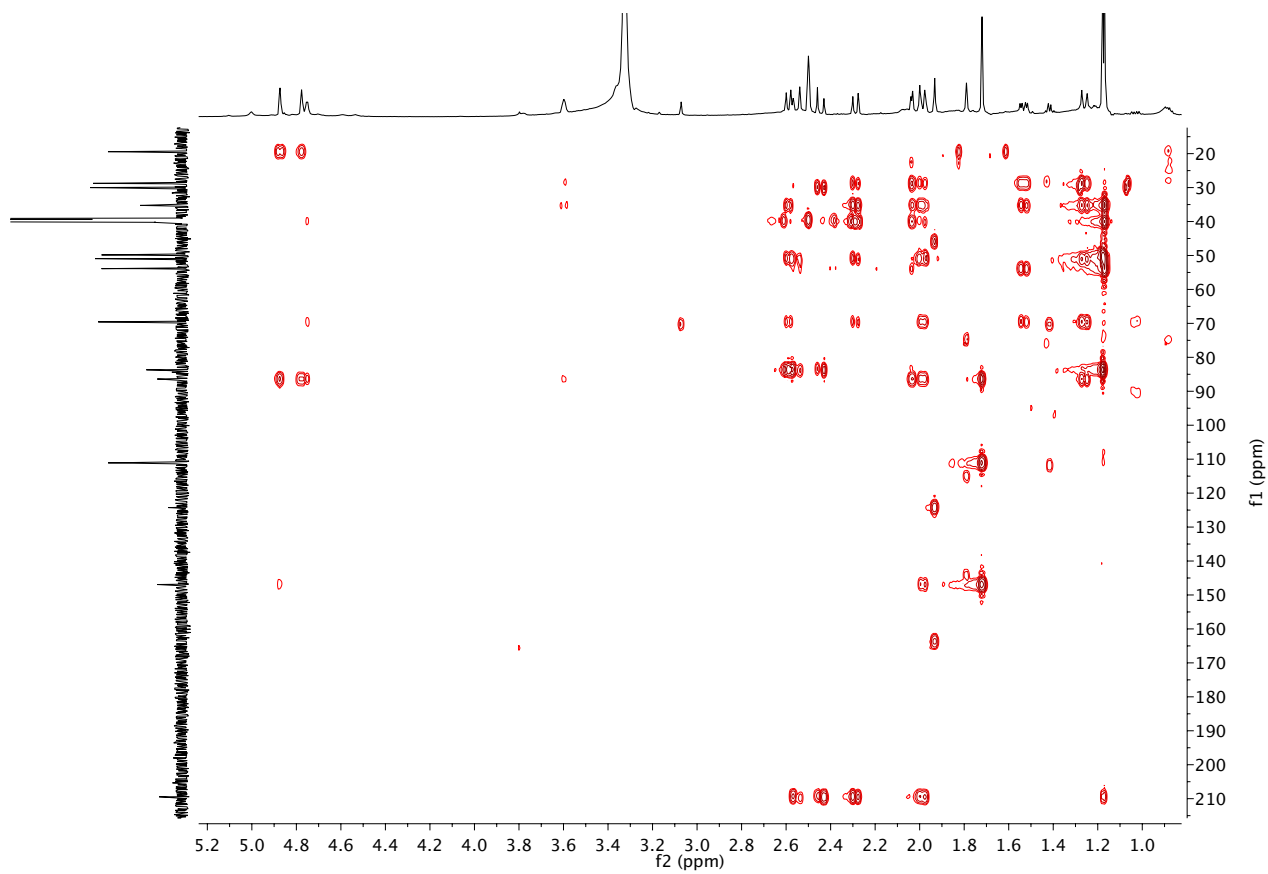


Figure S11. HMBC Spectrum of **2** in DMSO- d_6

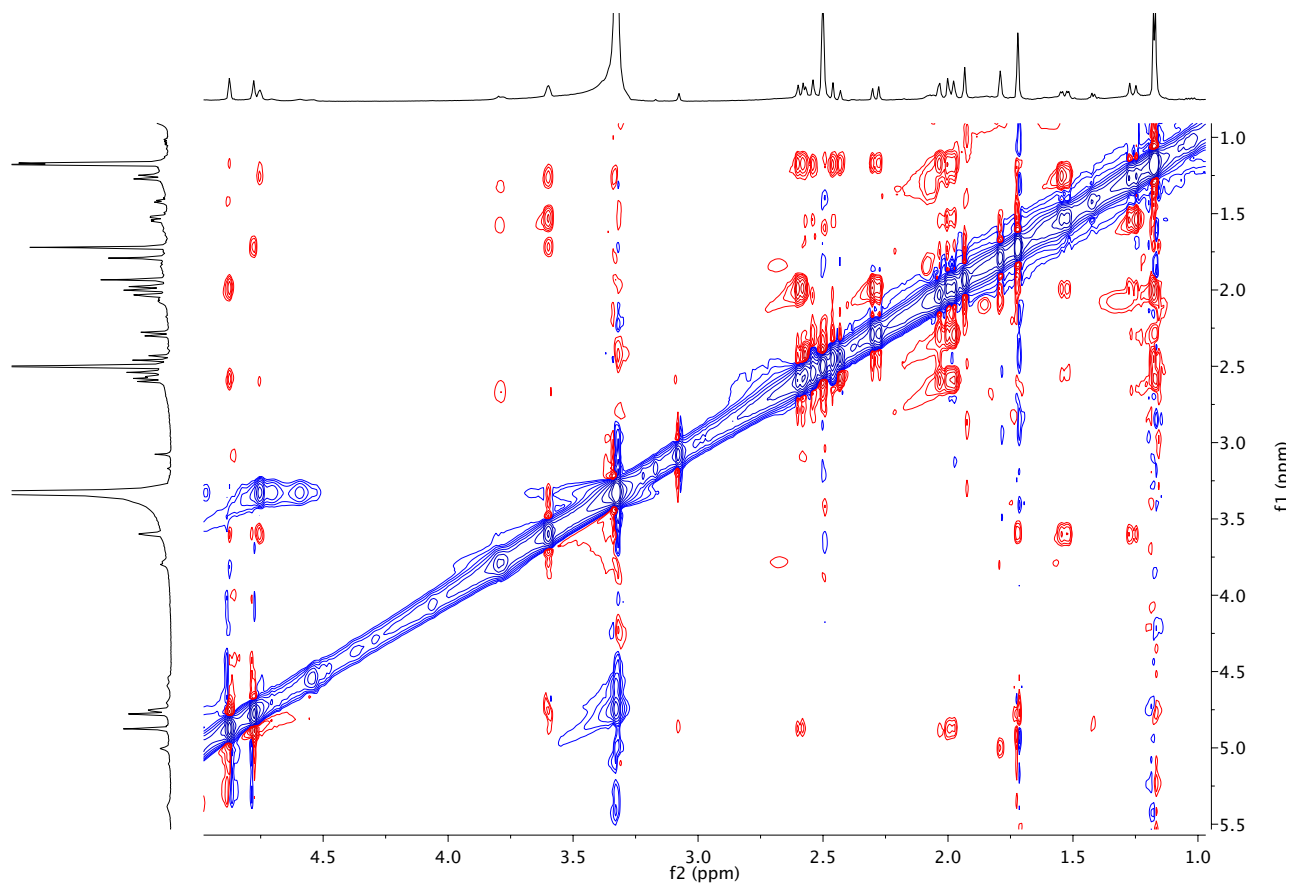


Figure S12. 2D ROESY Spectra of **2** in DMSO- d_6

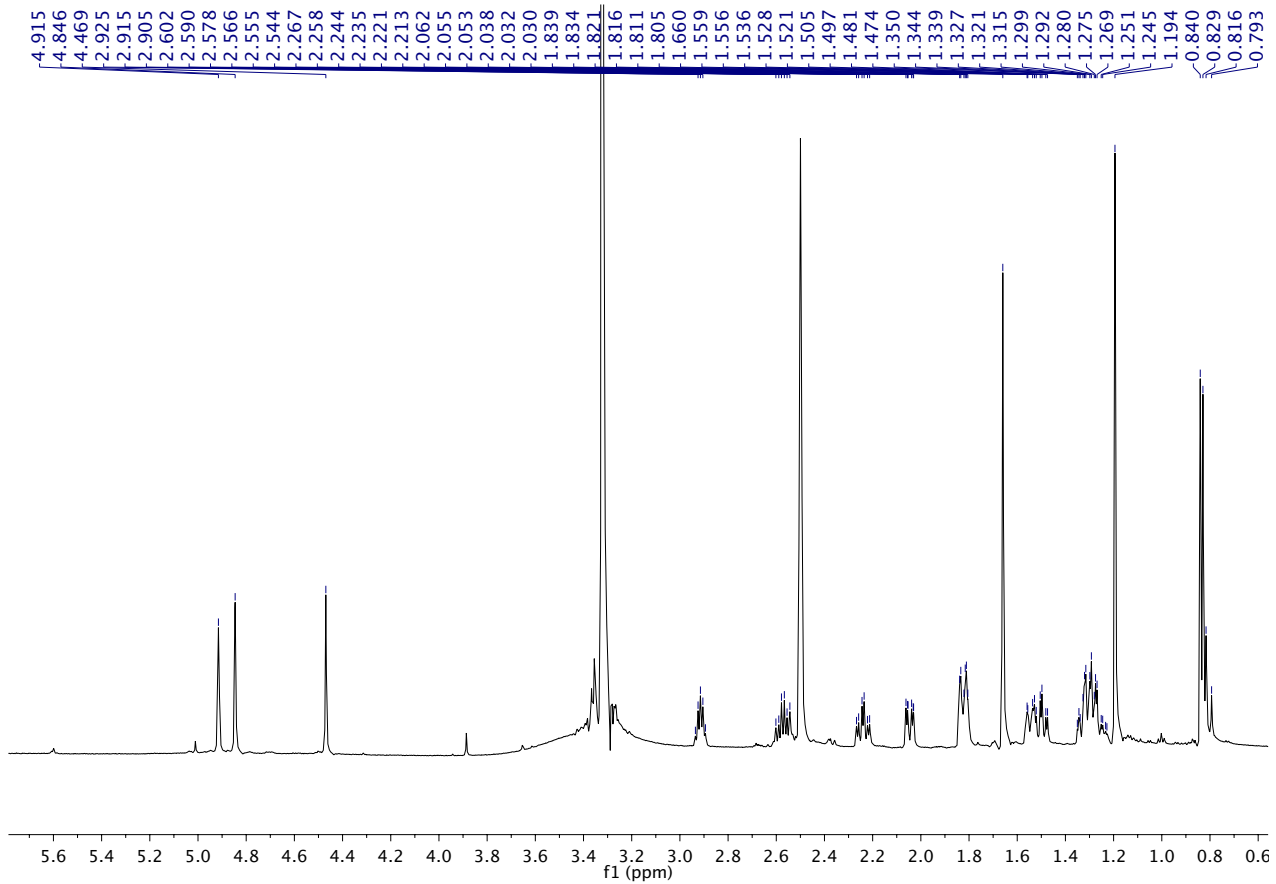


Figure S13. ^1H Spectrum of **3** in $\text{DMSO-}d_6$

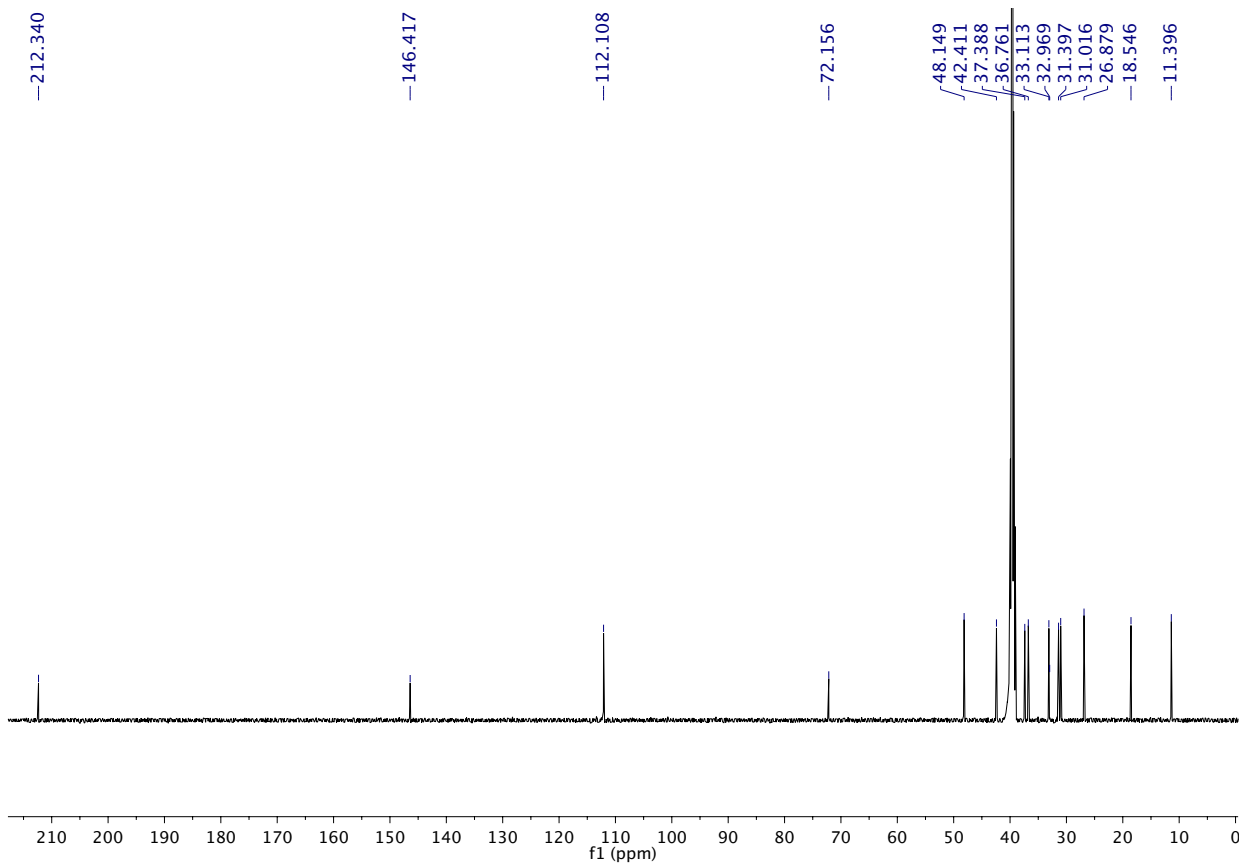


Figure S14. ^{13}C Spectrum of **3** in $\text{DMSO-}d_6$

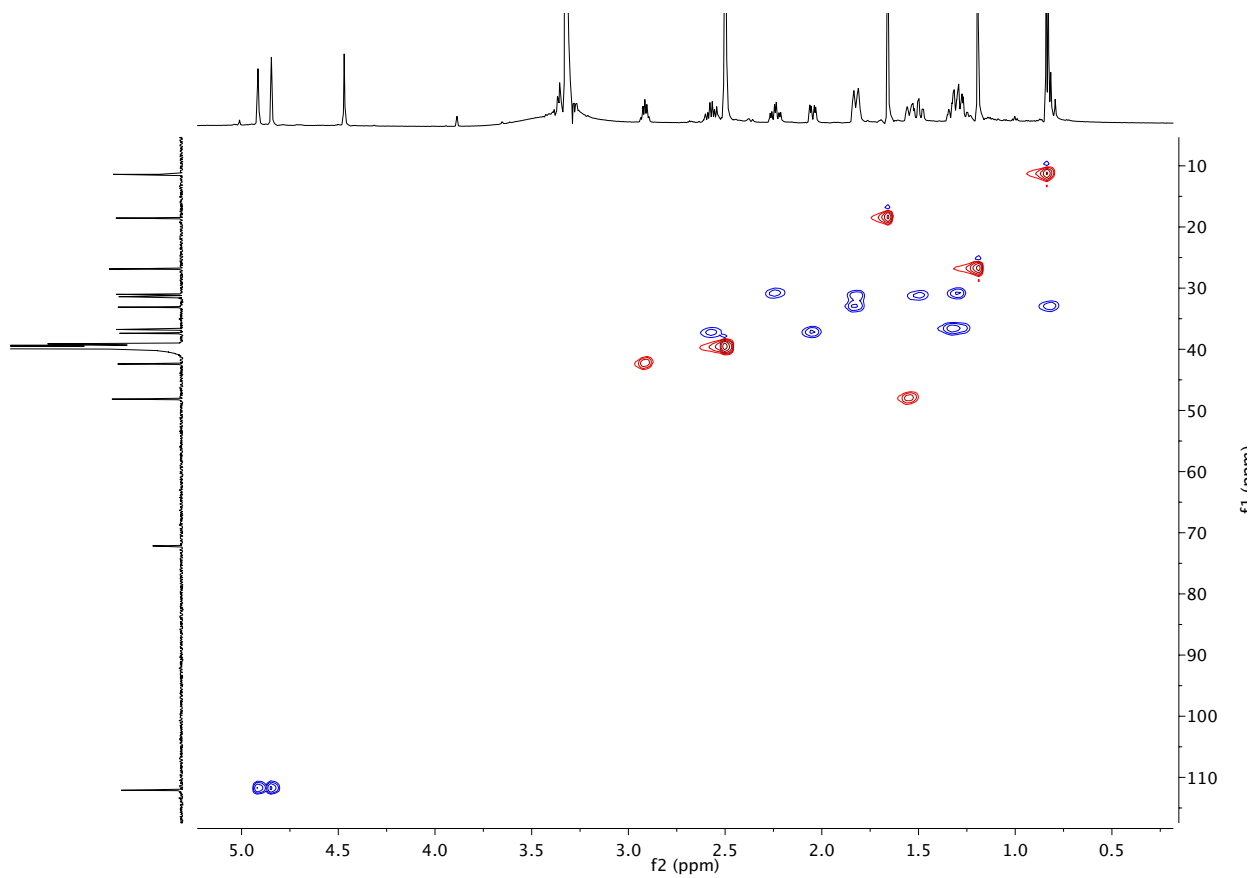


Figure S15. HSQC Spectrum of **3** in DMSO-*d*₆

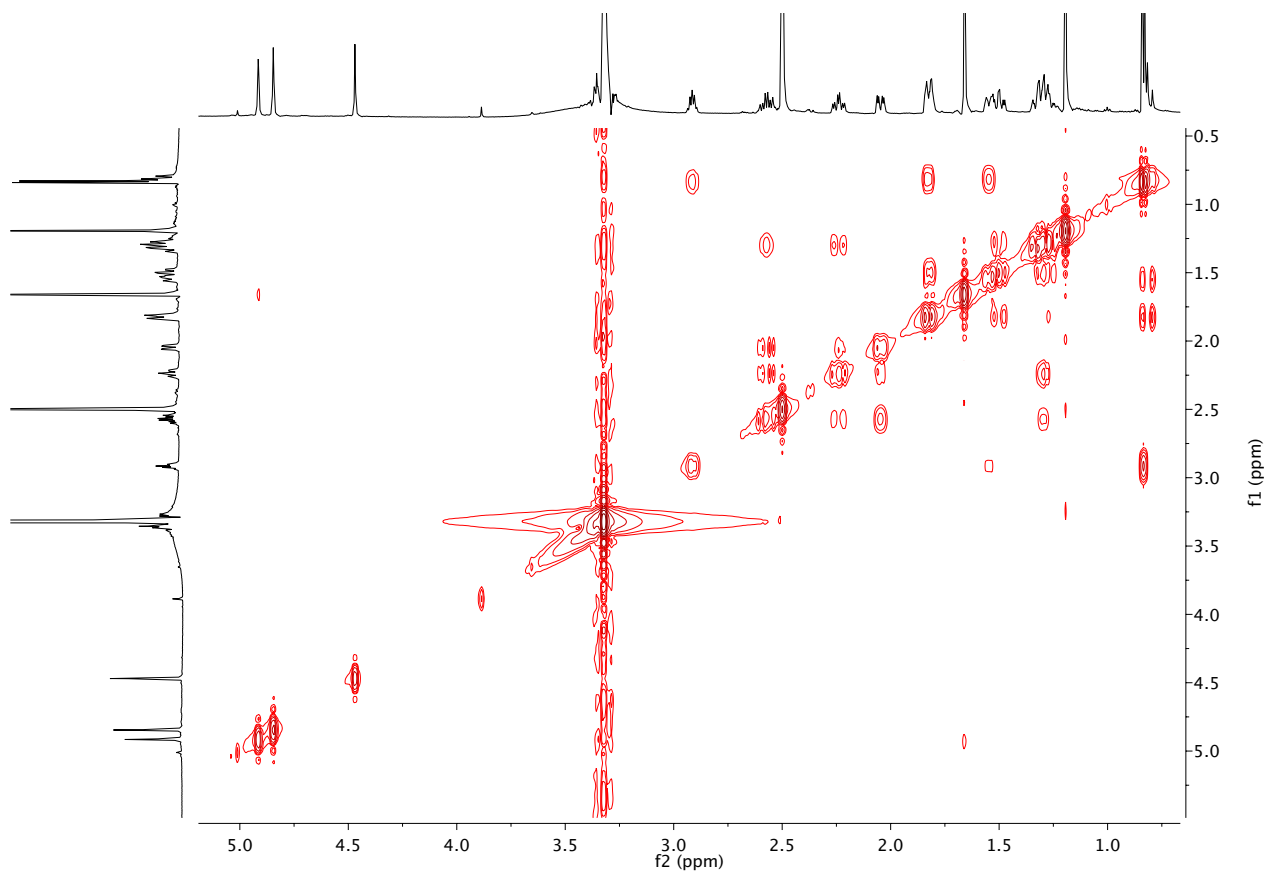


Figure S16. COSY Spectrum of **3** in DMSO-*d*₆

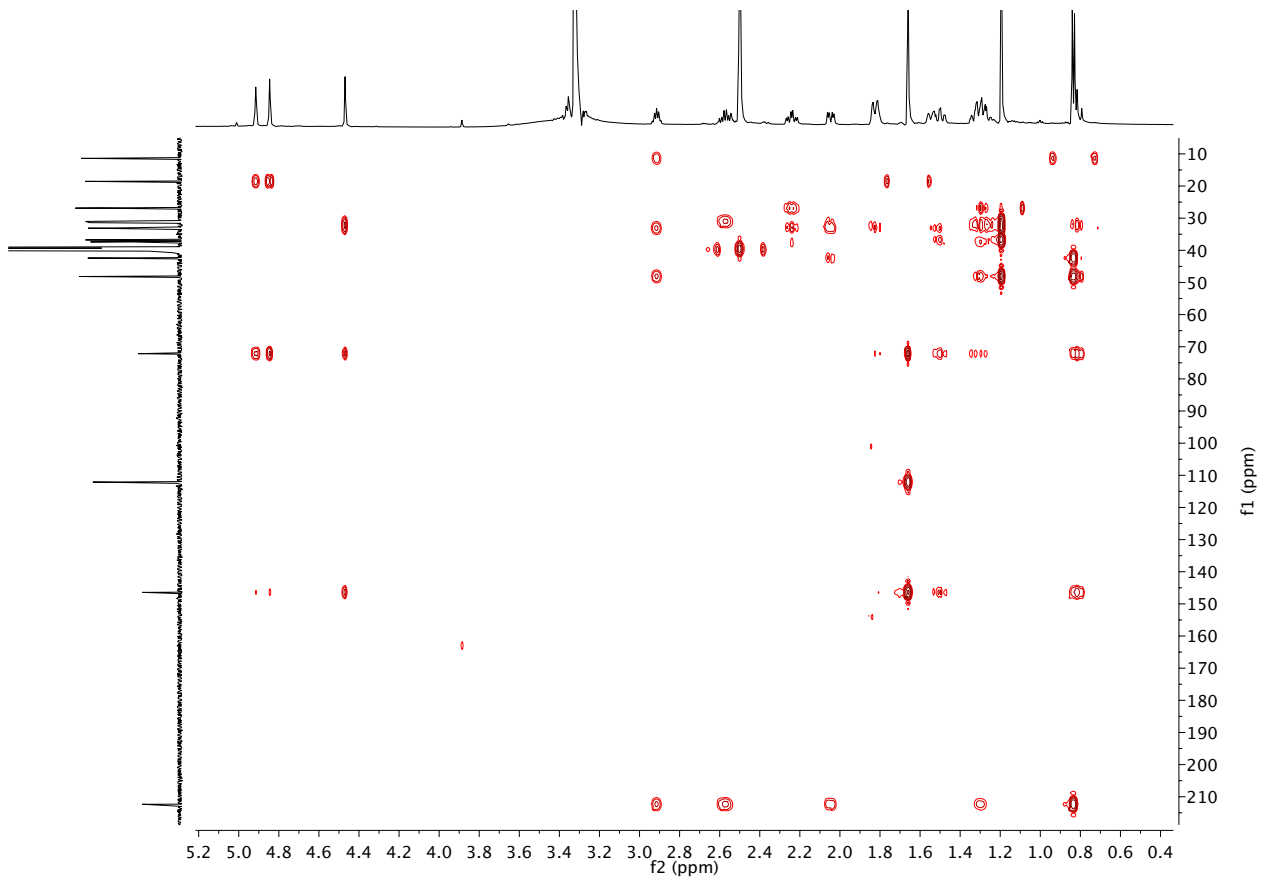


Figure S17. HMBC Spectrum of **3** in DMSO- d_6

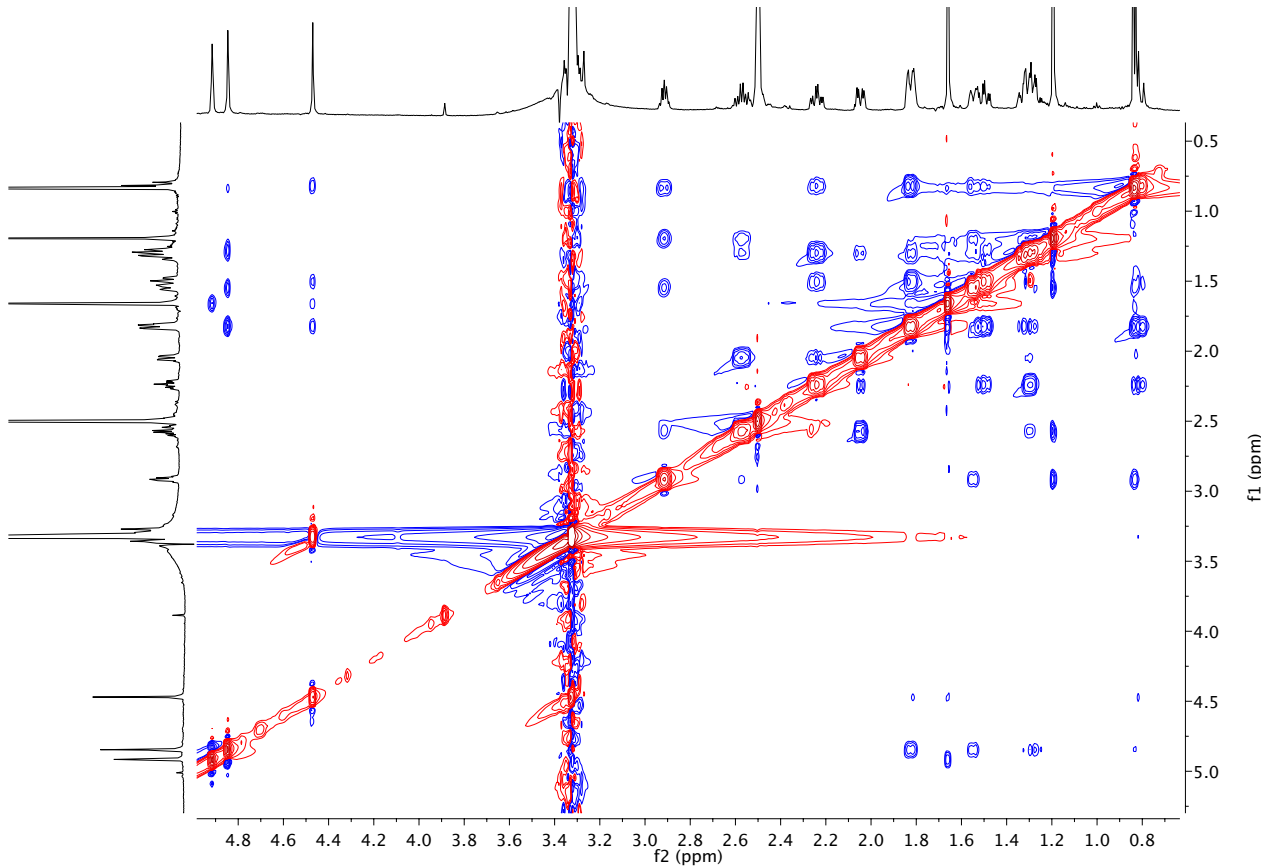


Figure S18. 2D NOESY Spectra of **3** in DMSO- d_6

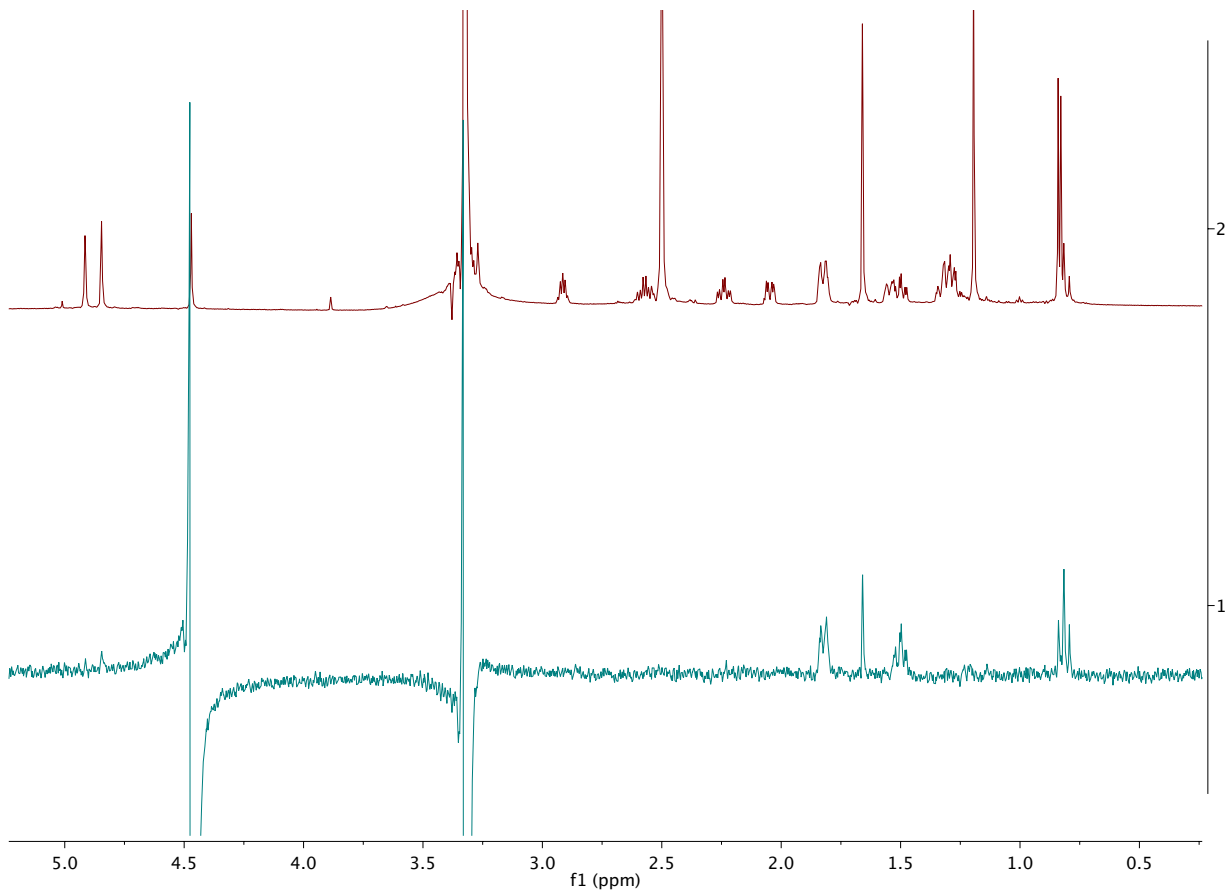


Figure S19. 1D NOESY Spectrum of **3** (irradiated at 4.47ppm) in DMSO- d_6

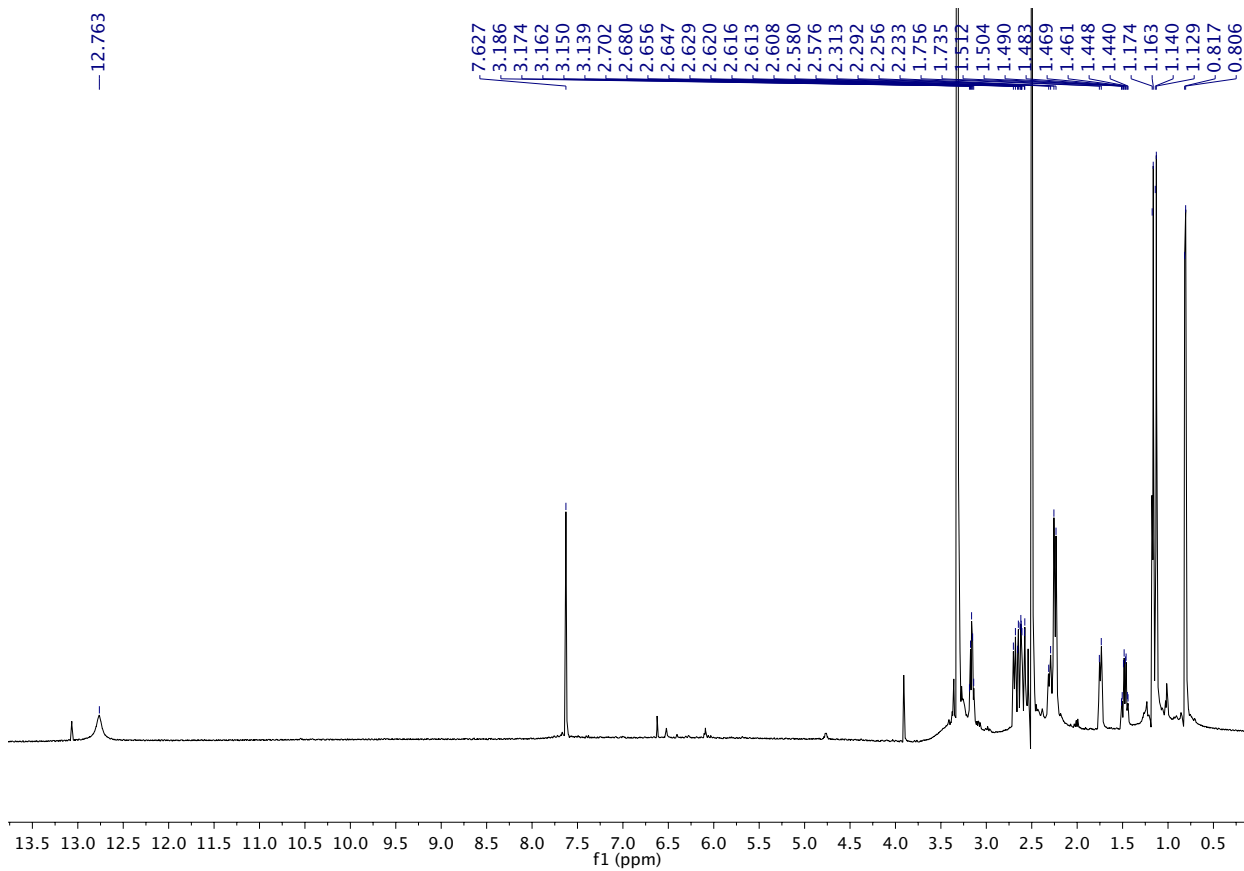


Figure S20. ^1H Spectrum of **4** in DMSO- d_6

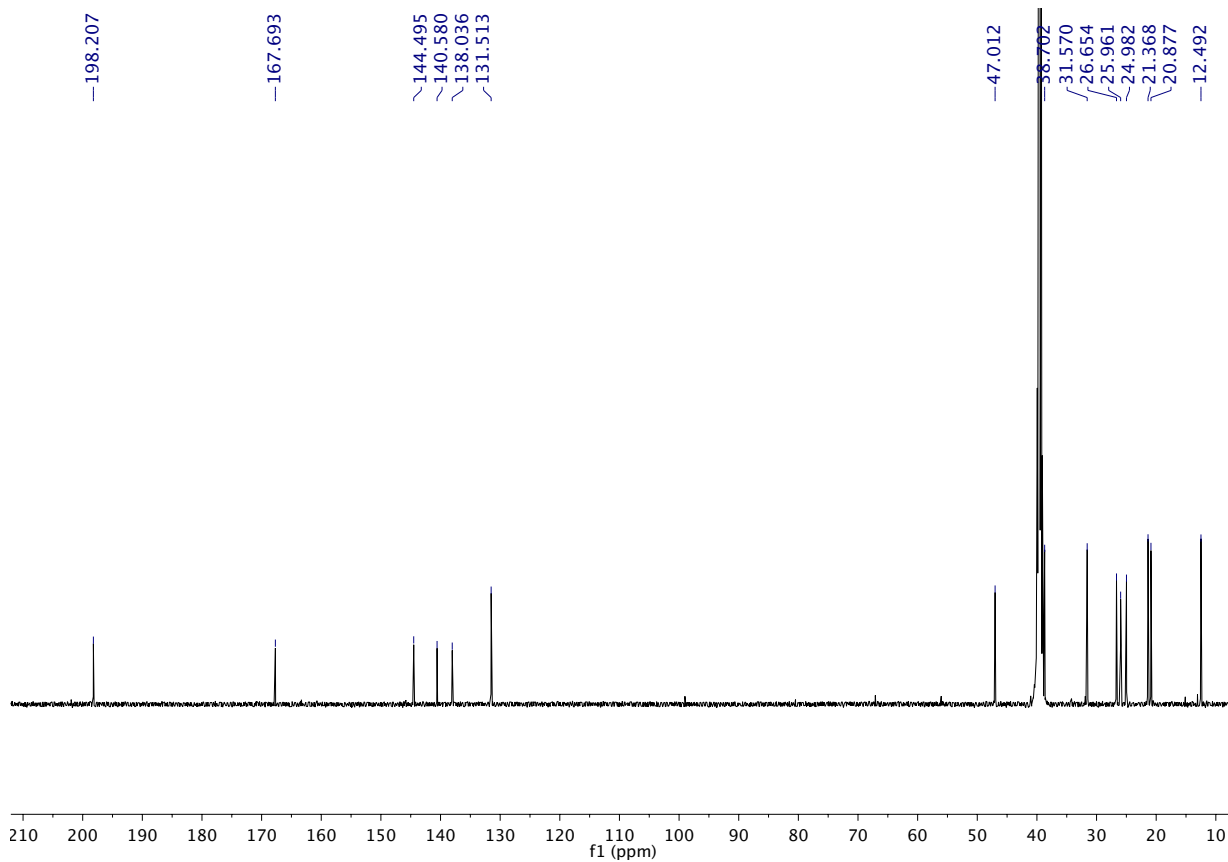


Figure S21. ^{13}C Spectrum of **4** in $\text{DMSO-}d_6$

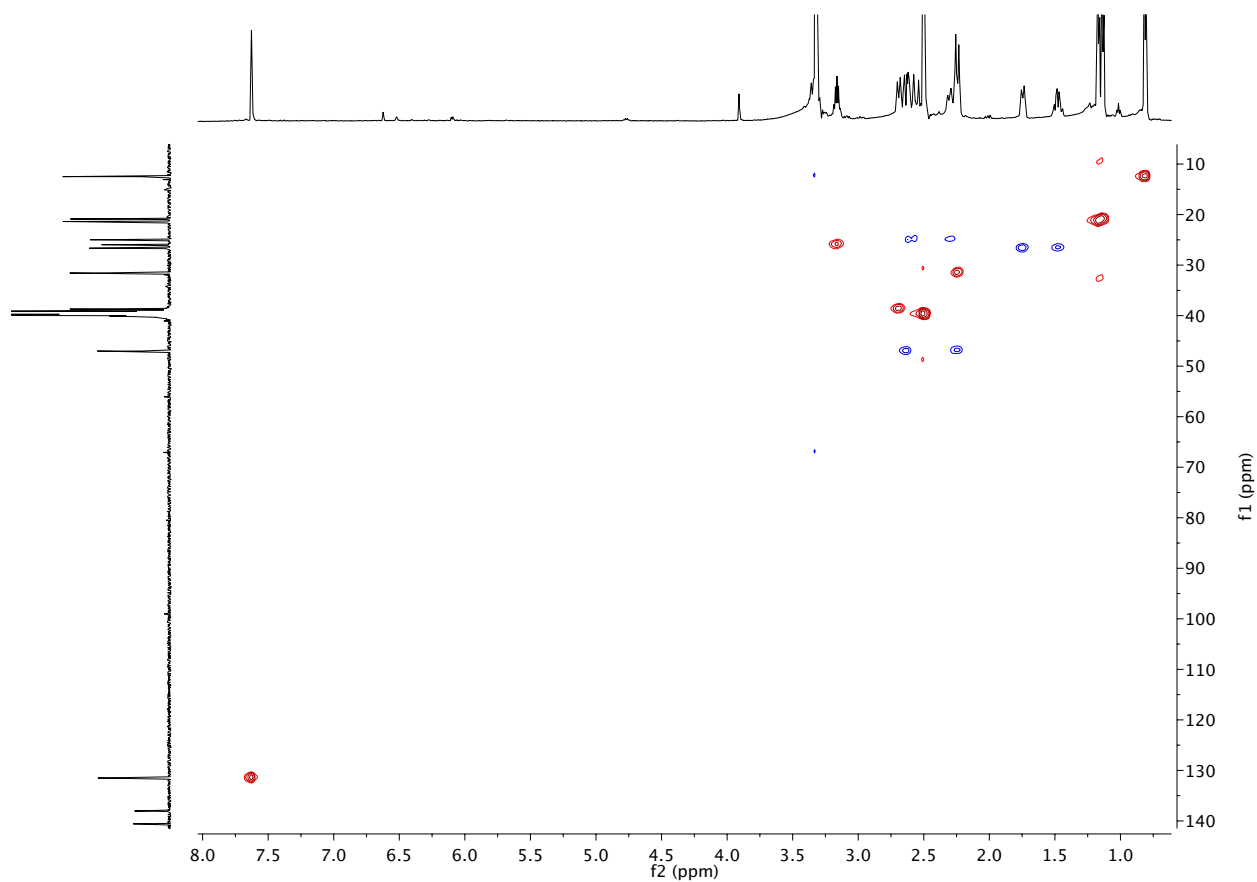


Figure S22. HSQC Spectrum of **4** in $\text{DMSO-}d_6$

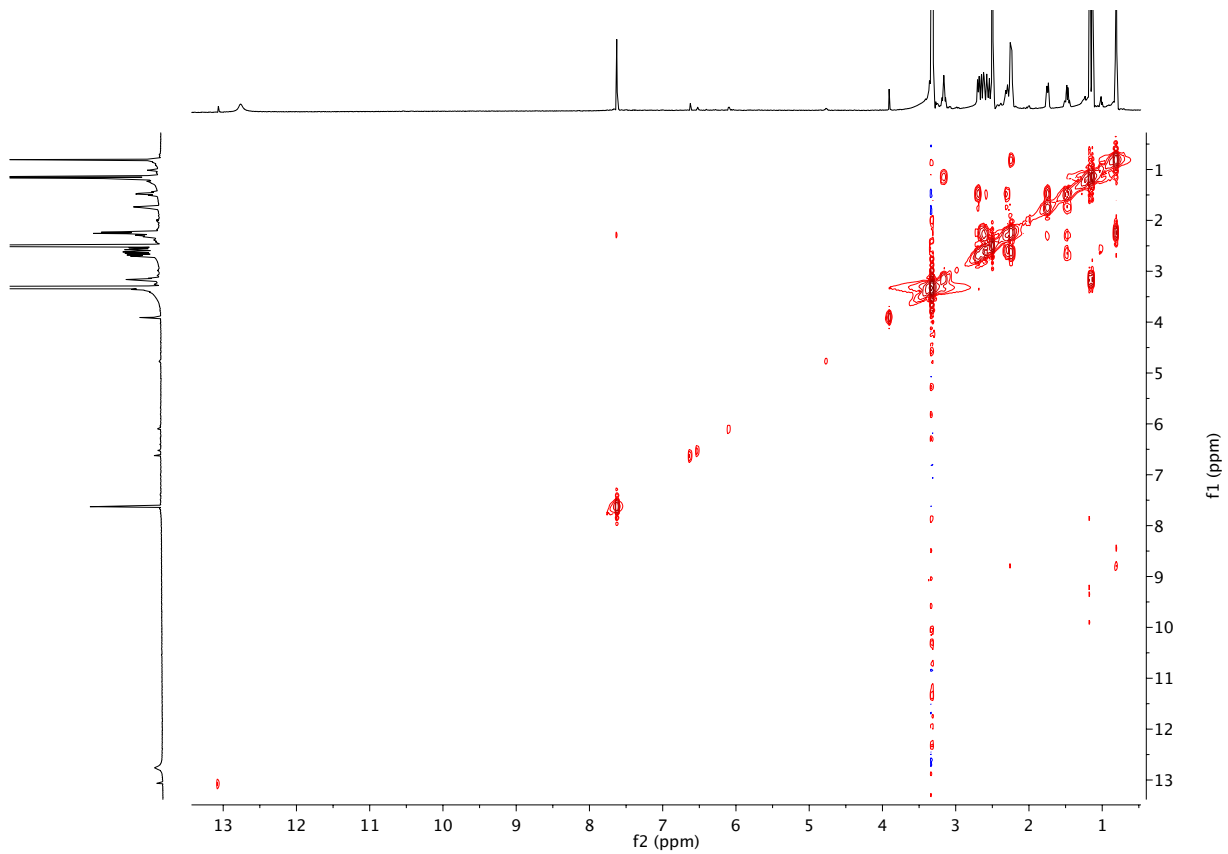


Figure S23. COSY Spectrum of **4** in DMSO-*d*₆

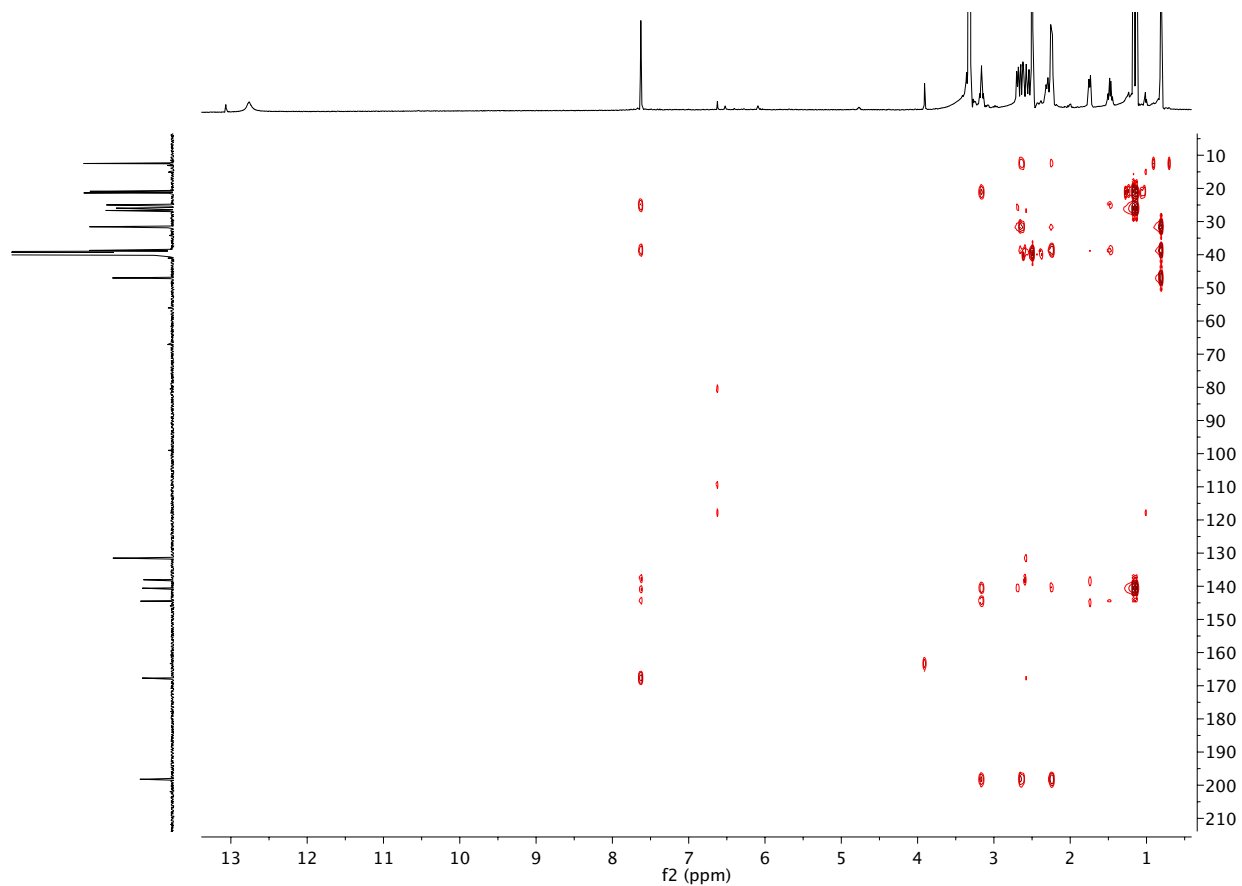


Figure S24. HMBC Spectrum of **4** in DMSO-*d*₆

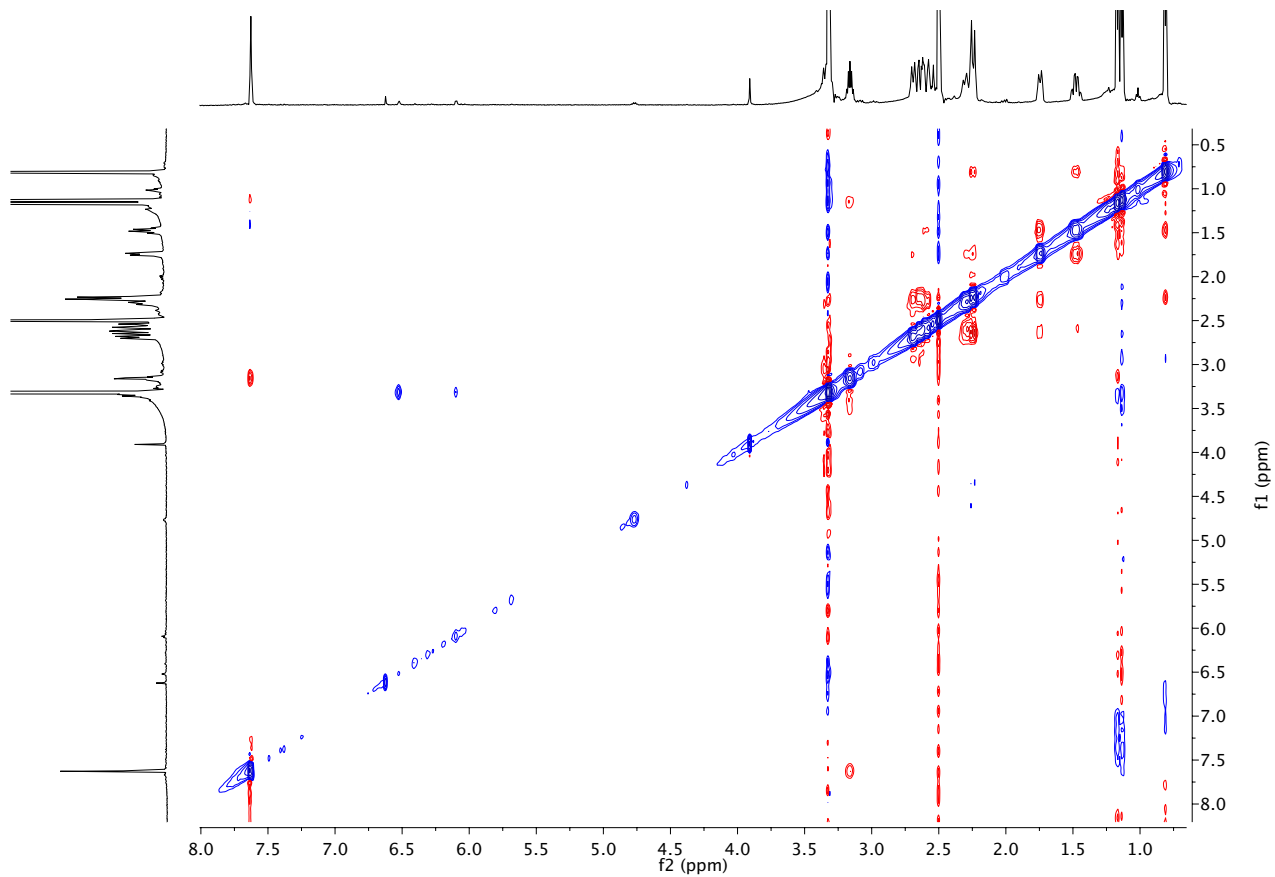


Figure S25. 2D ROESY Spectra of **4** in DMSO- d_6

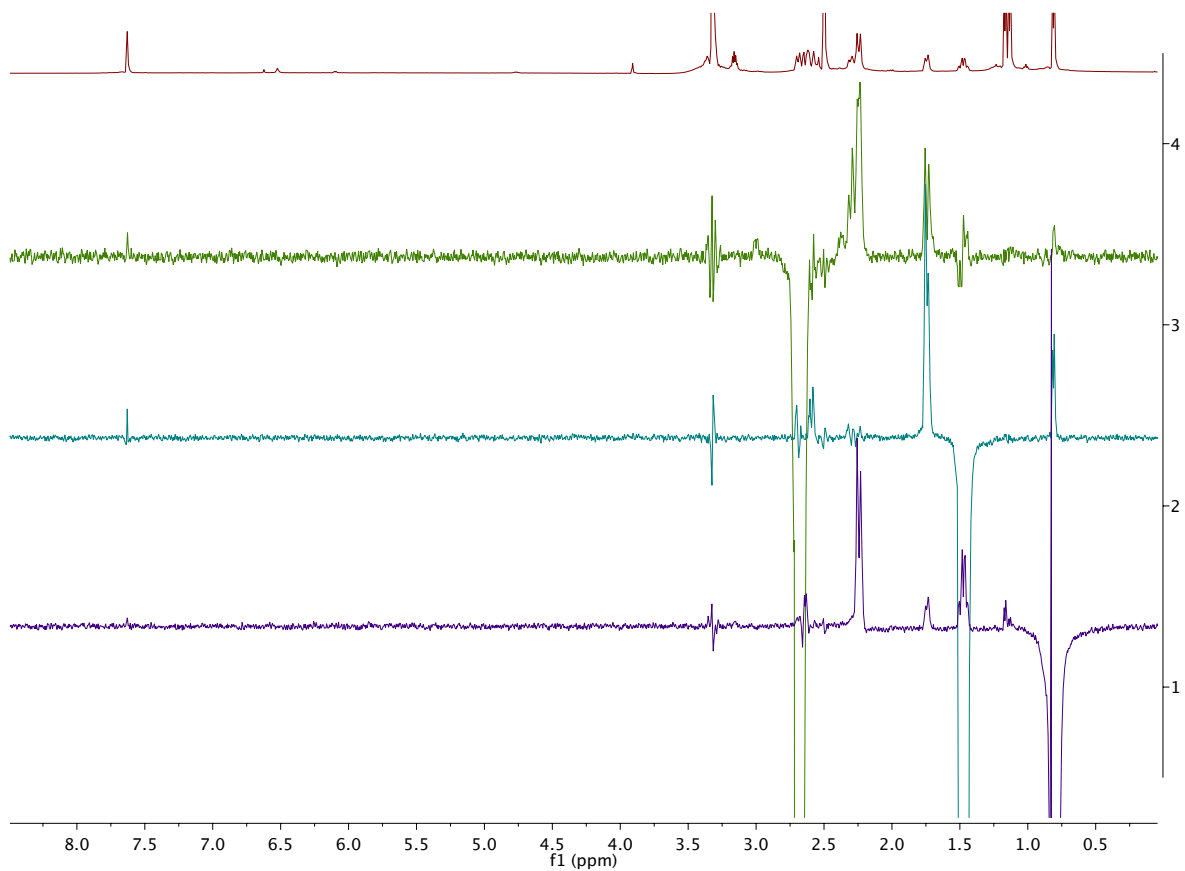


Figure S26. 1D NOESY Spectra of **4** in DMSO- d_6

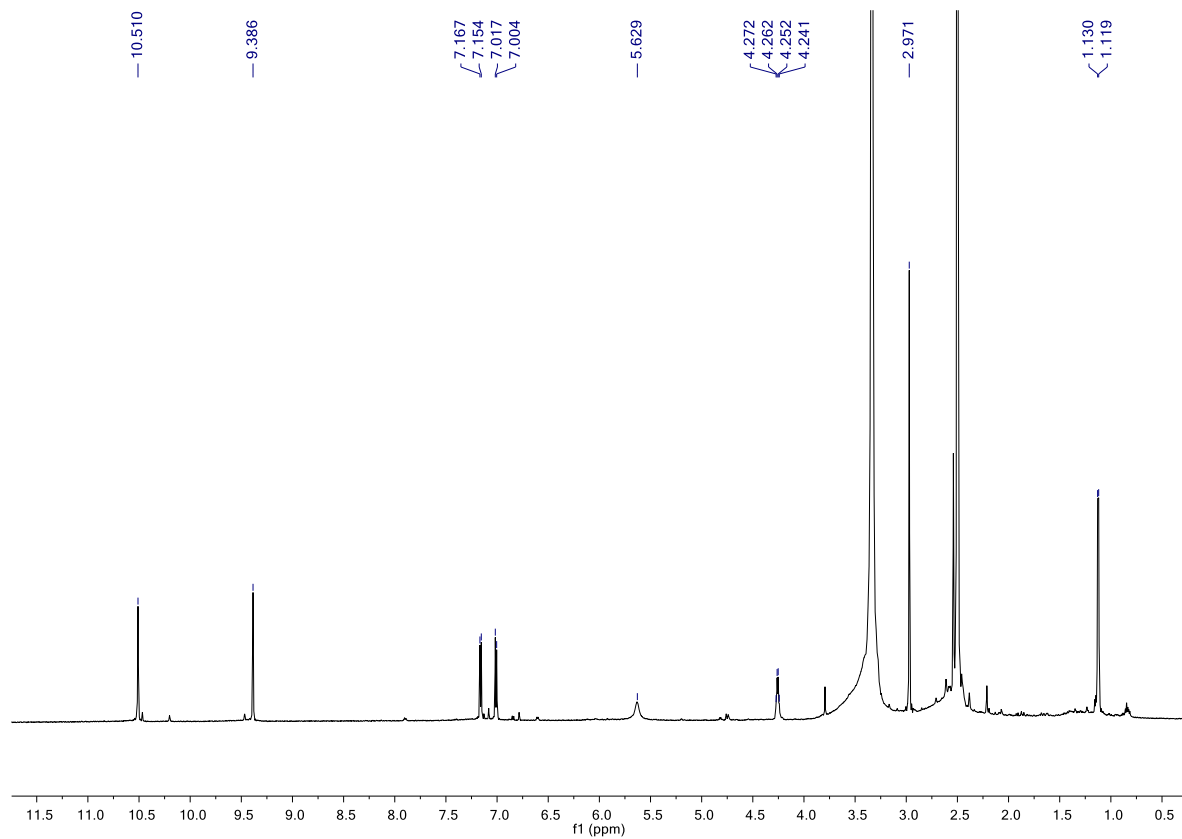


Figure S27. ^1H Spectrum of **5** in $\text{DMSO-}d_6$

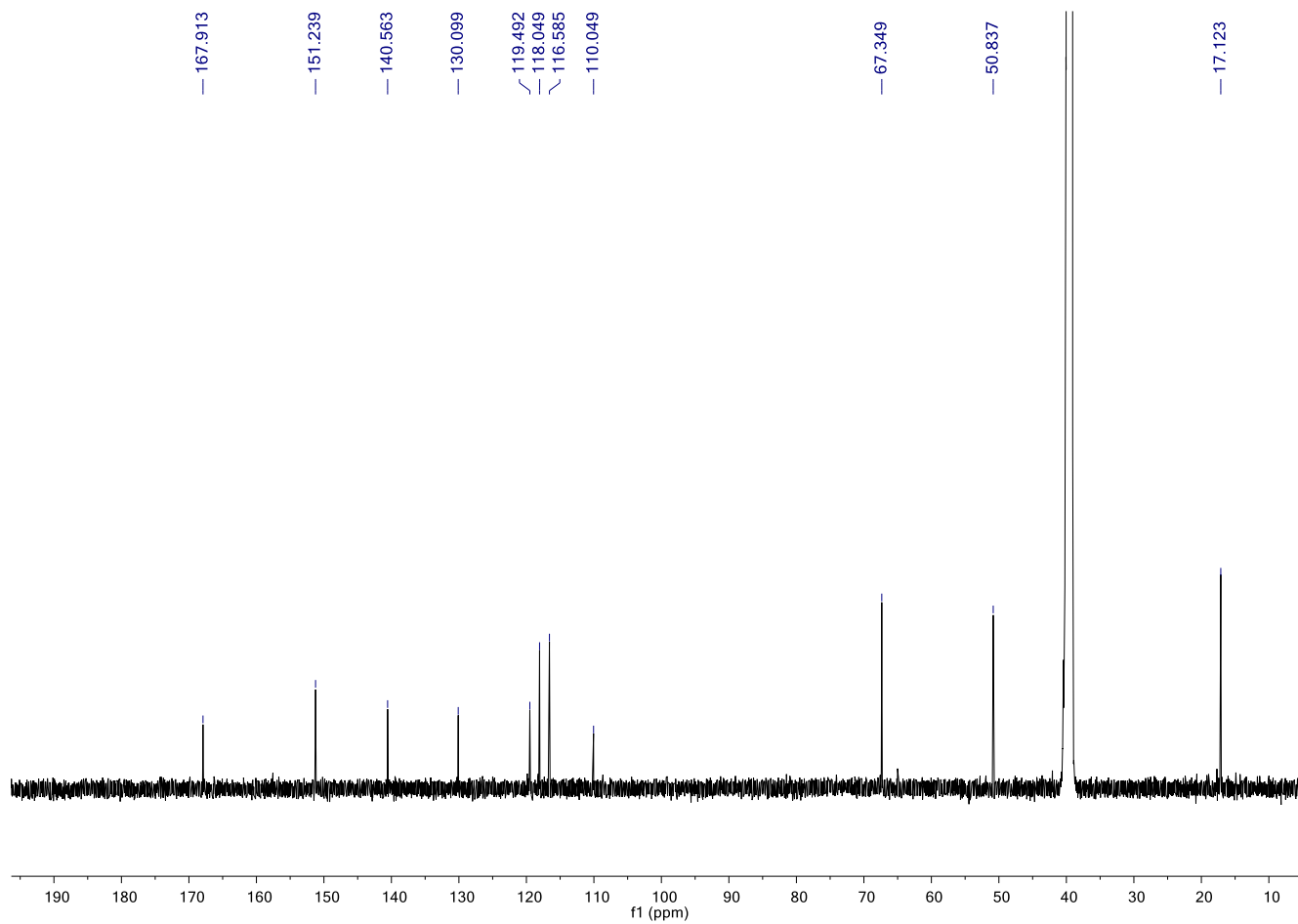


Figure S28. ^{13}C Spectrum of **5** in $\text{DMSO-}d_6$

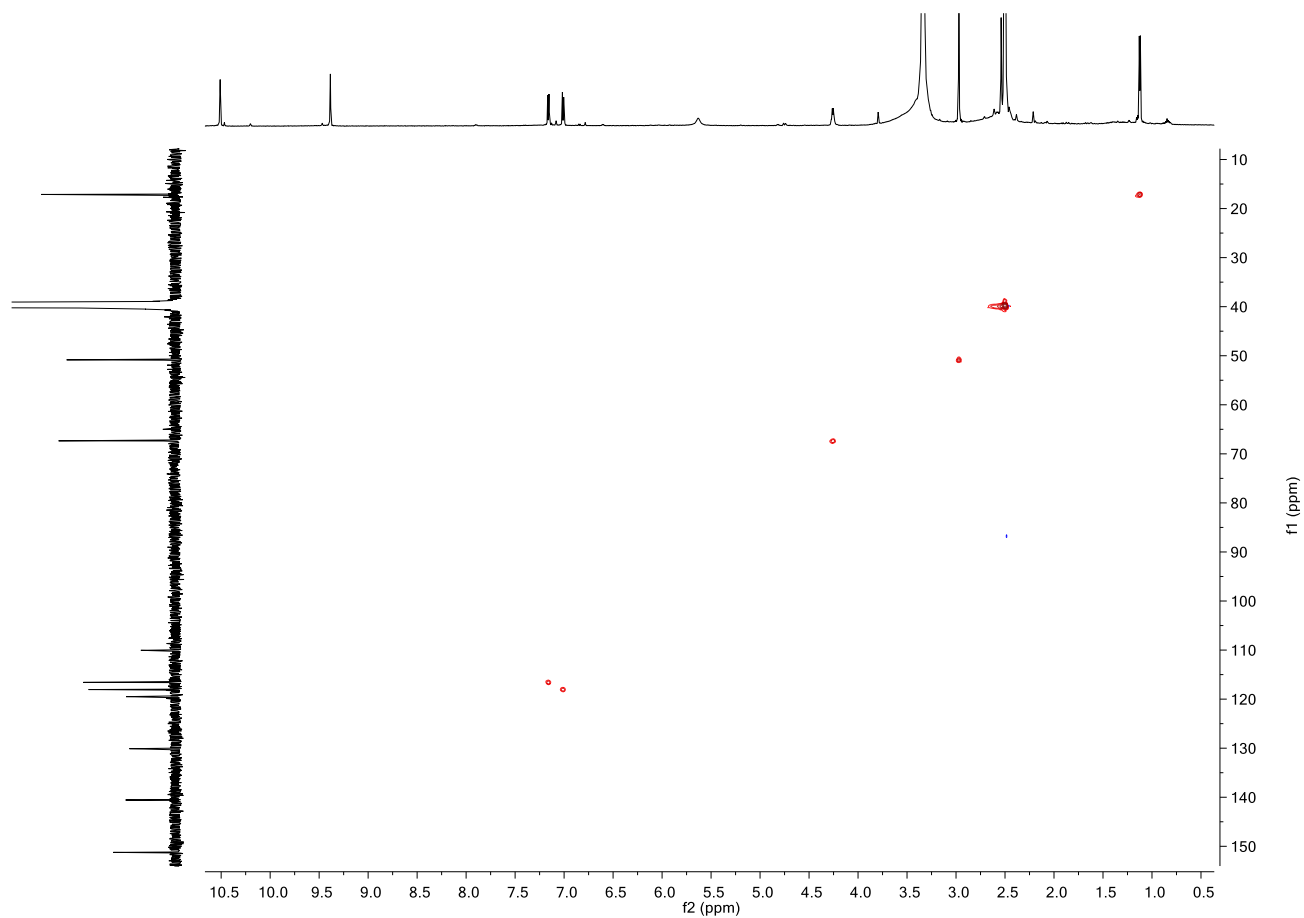


Figure S29. HSQC Spectrum of **5** in DMSO- d_6

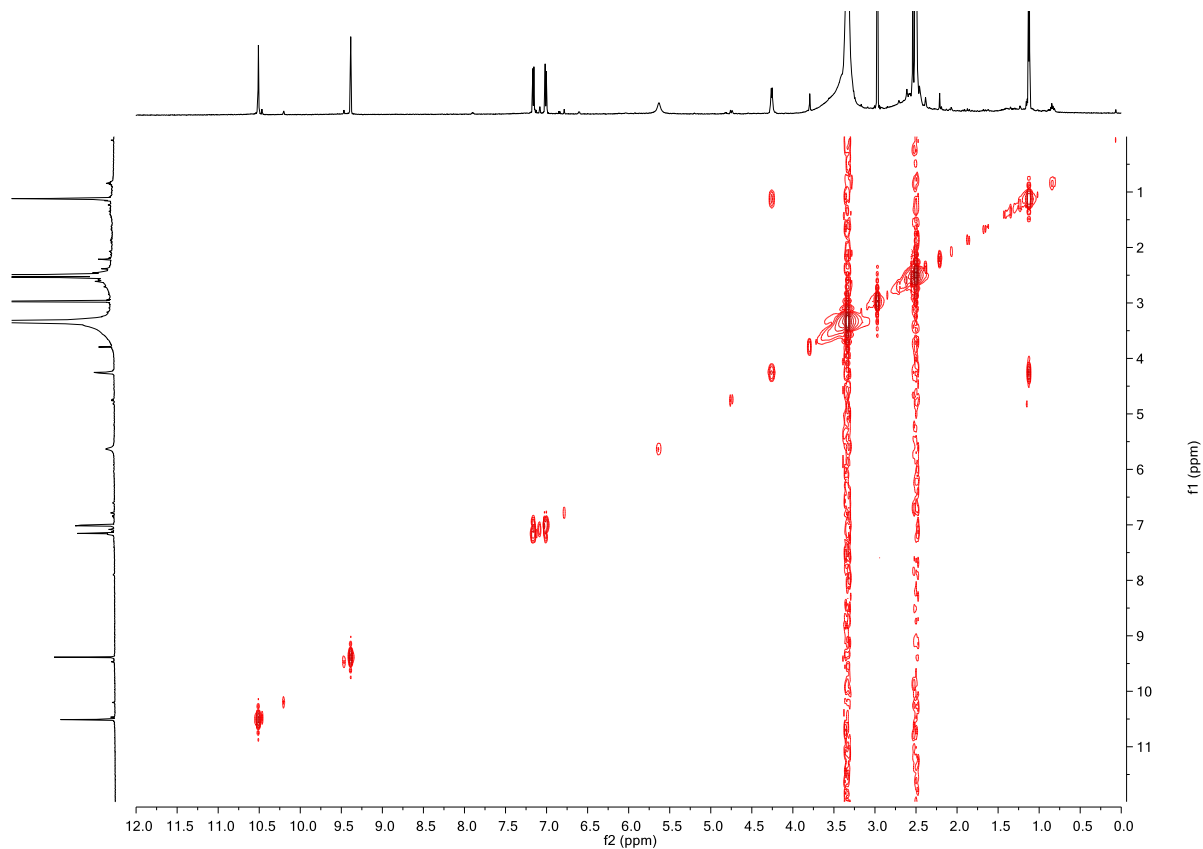


Figure S30. COSY Spectrum of **5** in DMSO- d_6

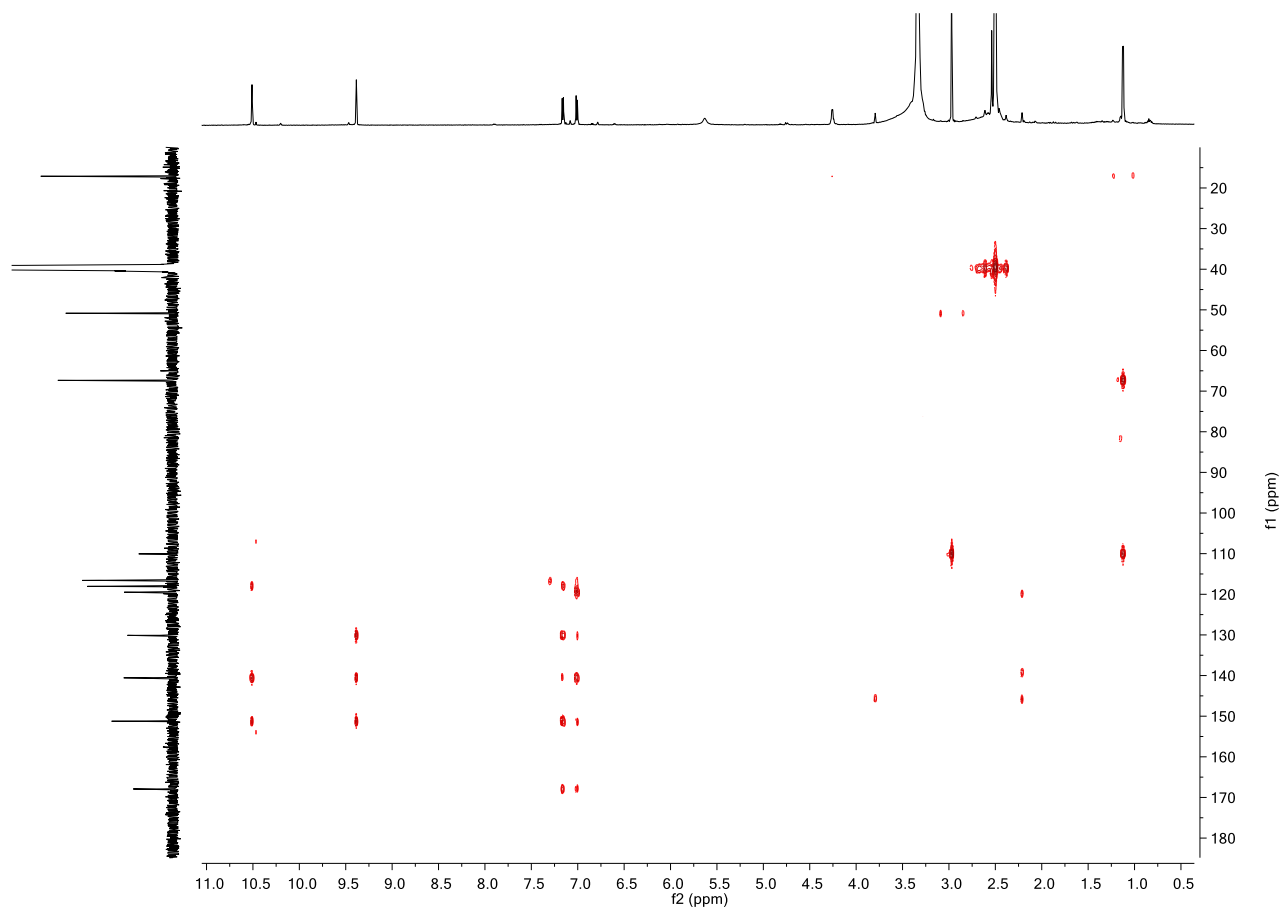


Figure S31. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **5** in DMSO- d_6

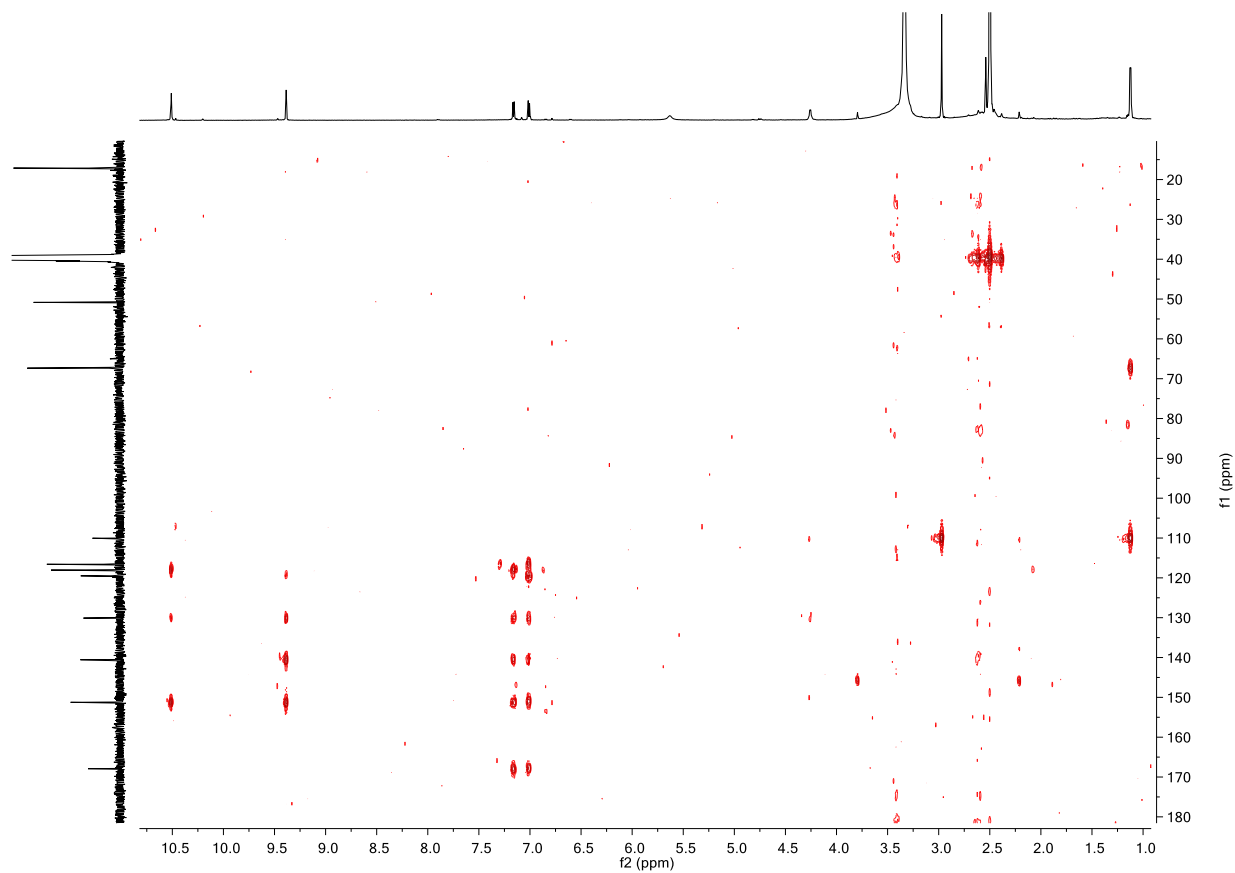


Figure S32. HMBC ($J_{\text{HC}} = 3$ Hz) Spectrum of **5** in DMSO- d_6

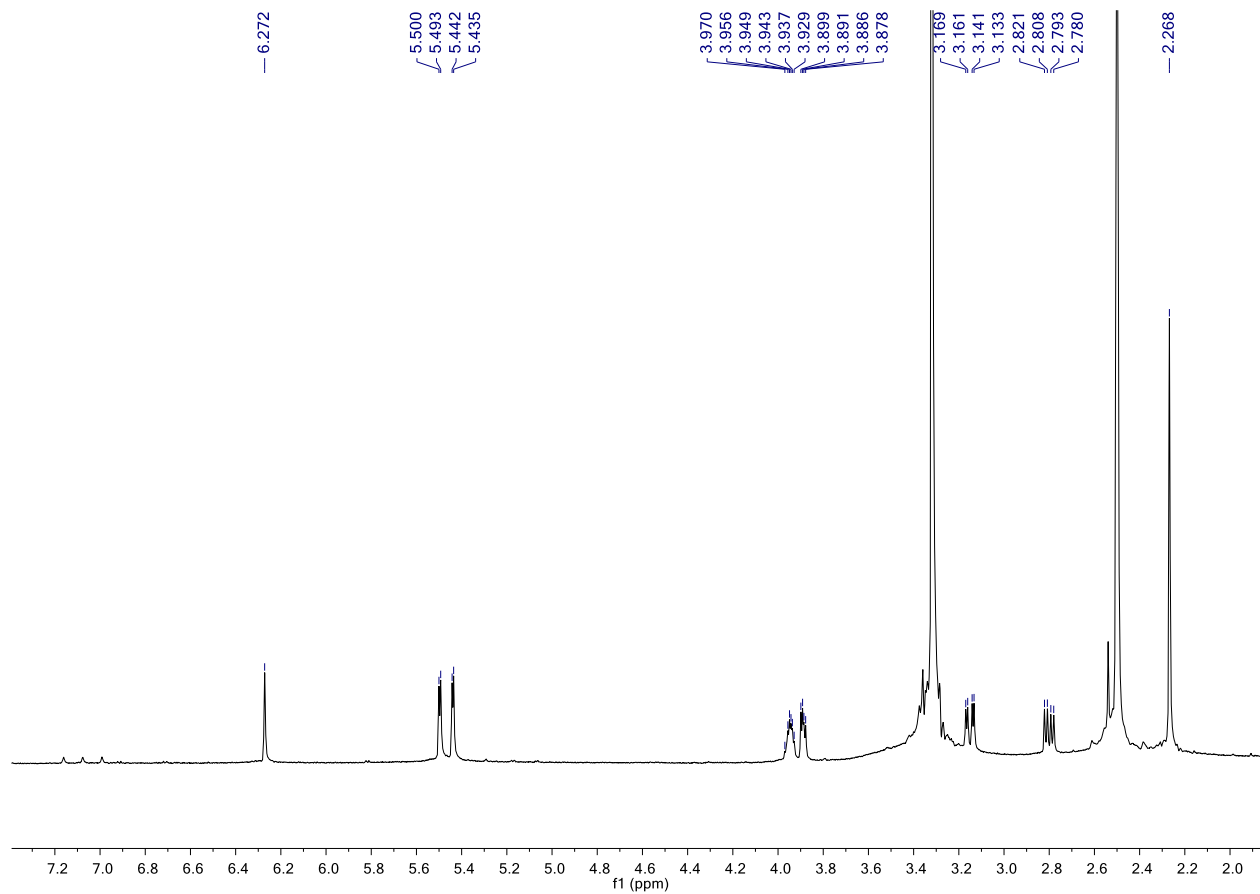


Figure S33. ^1H Spectrum of **6** in $\text{DMSO-}d_6$

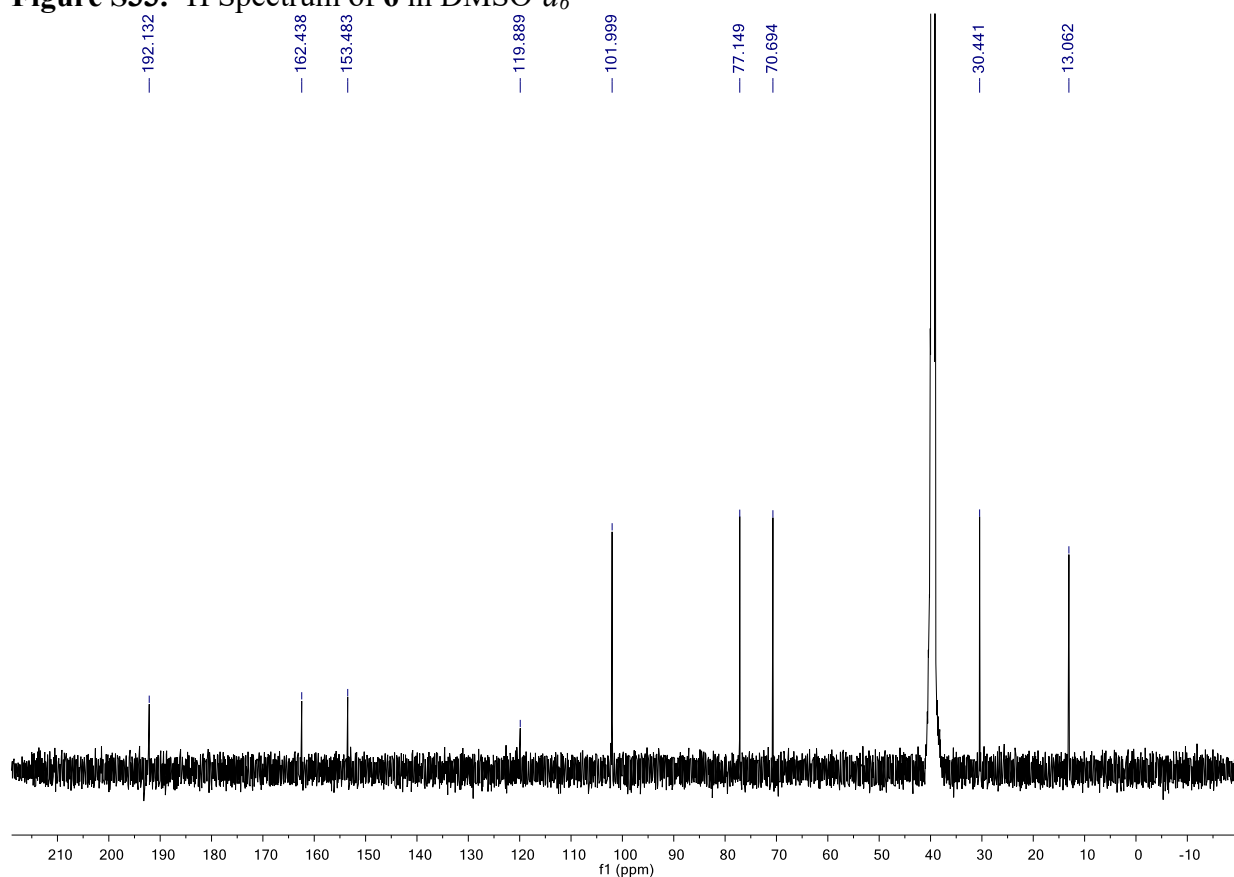


Figure S34. ^{13}C Spectrum of **6** in $\text{DMSO-}d_6$

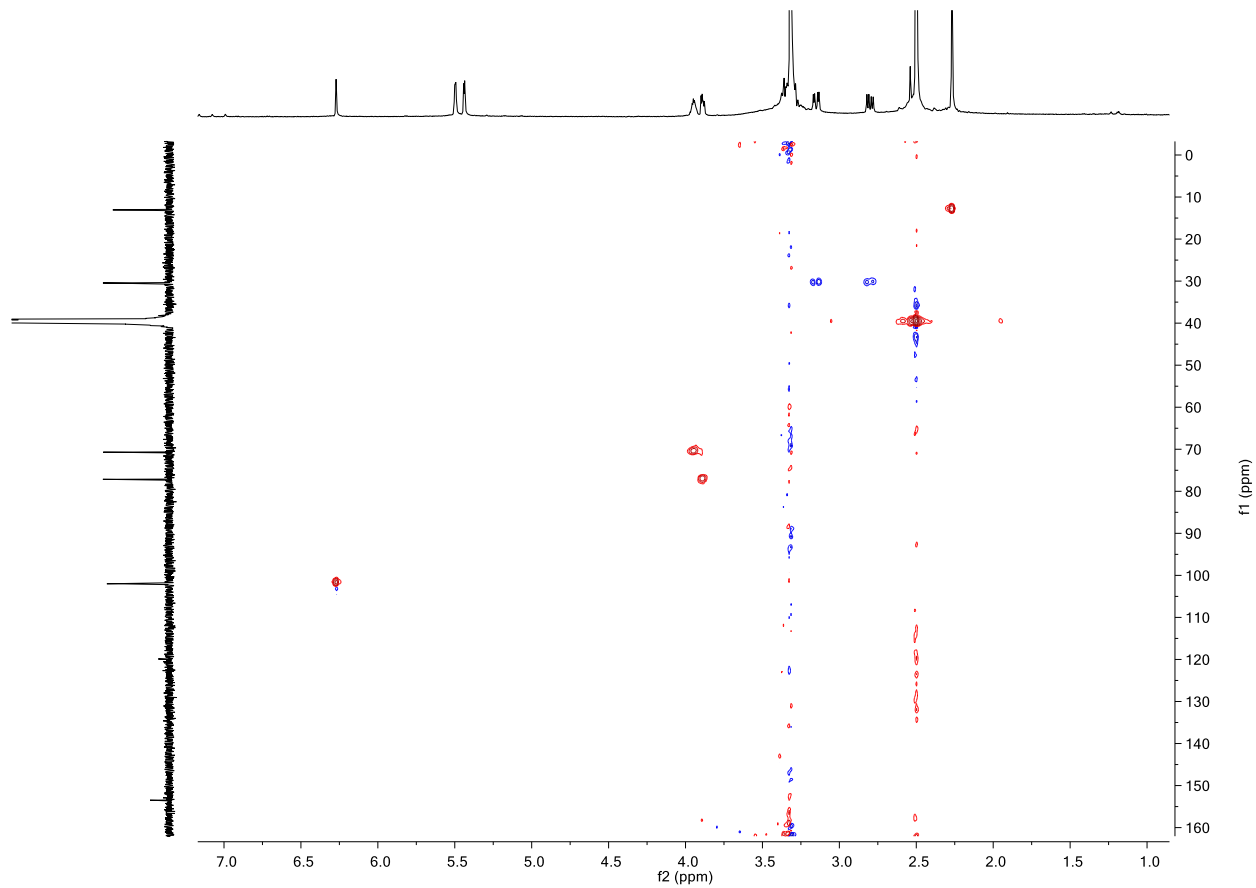


Figure S35. HSQC Spectrum of **6** in DMSO-*d*₆

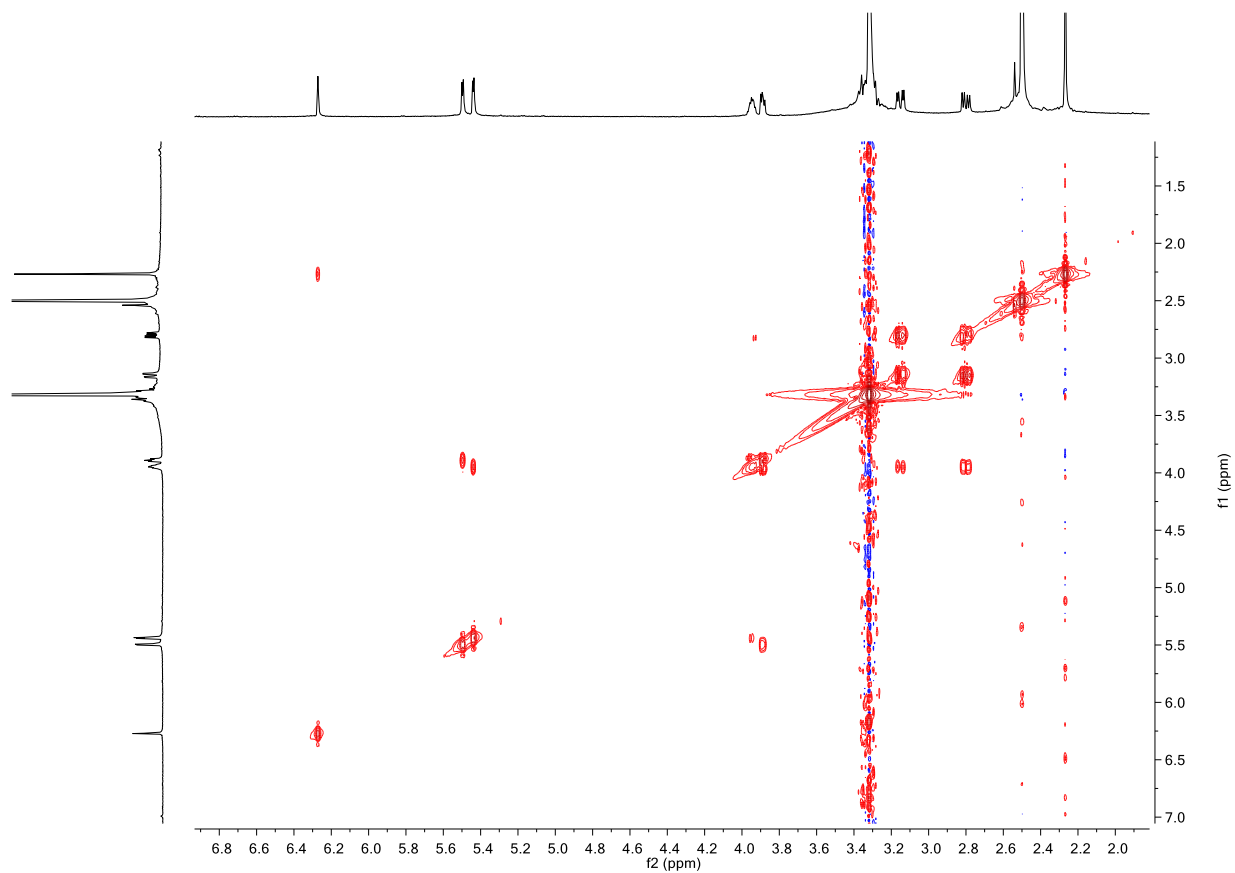


Figure S36. COSY Spectrum of **6** in DMSO-*d*₆

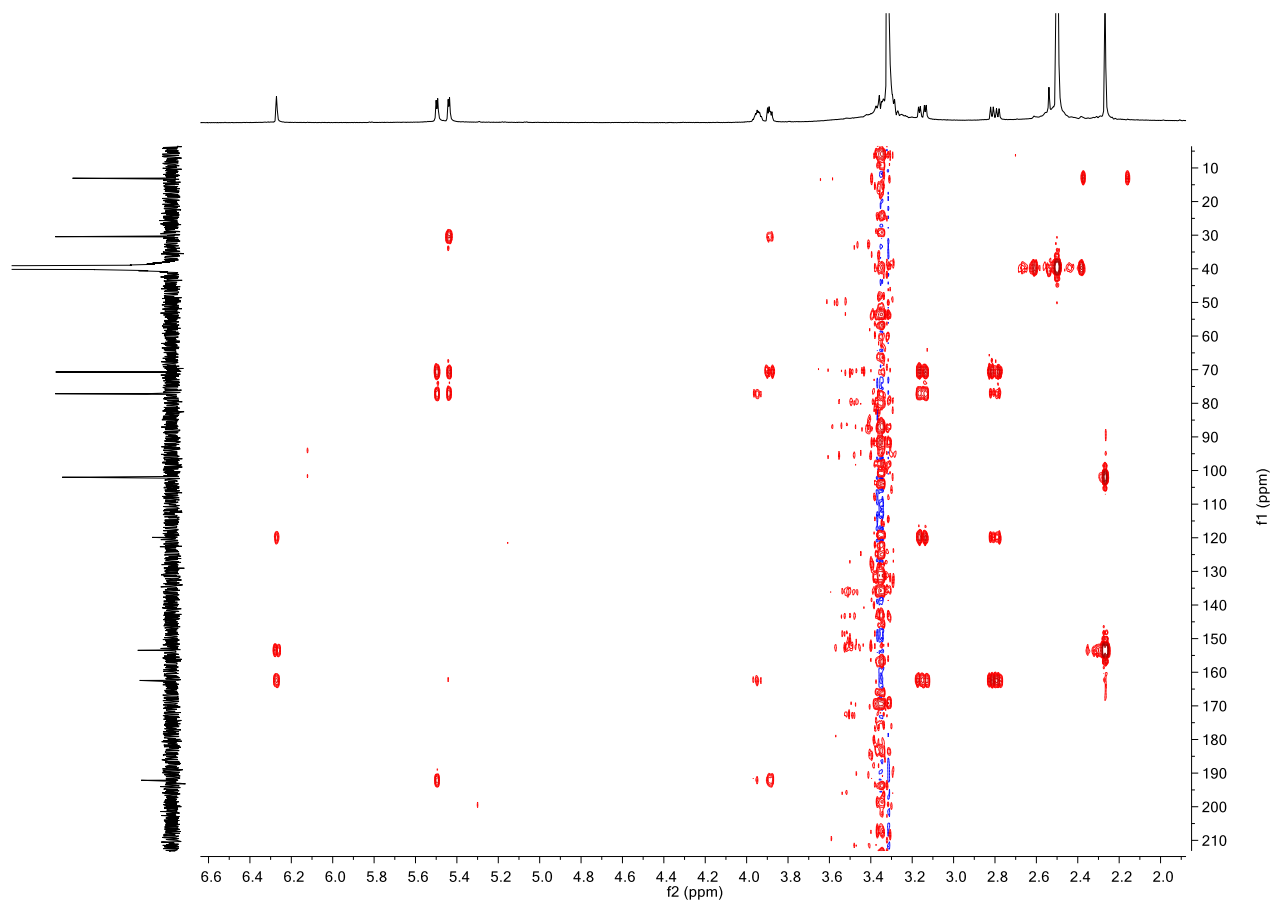


Figure S37. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **6** in DMSO-*d*₆

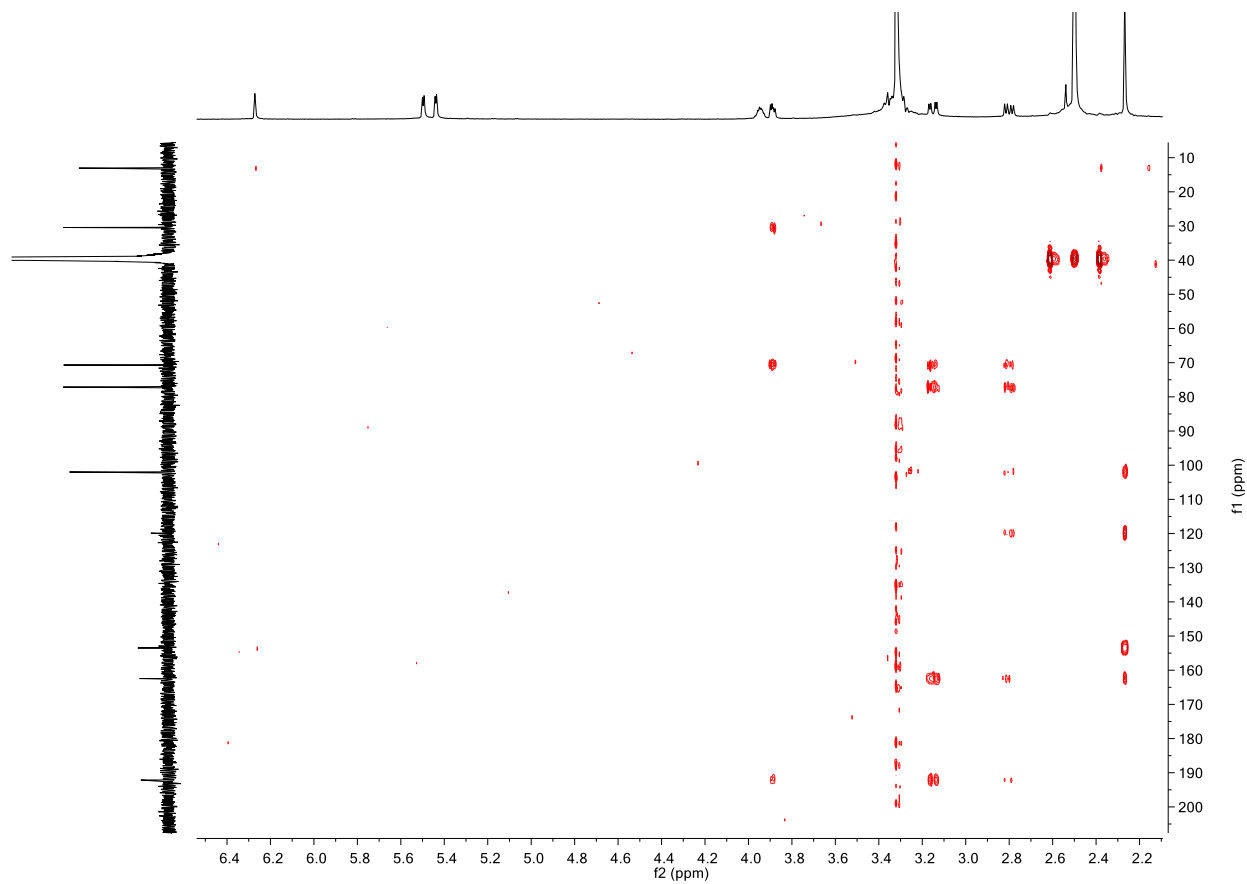


Figure S38. HMBC ($J_{\text{HC}} = 2$ Hz) Spectrum of **6** in DMSO-*d*₆

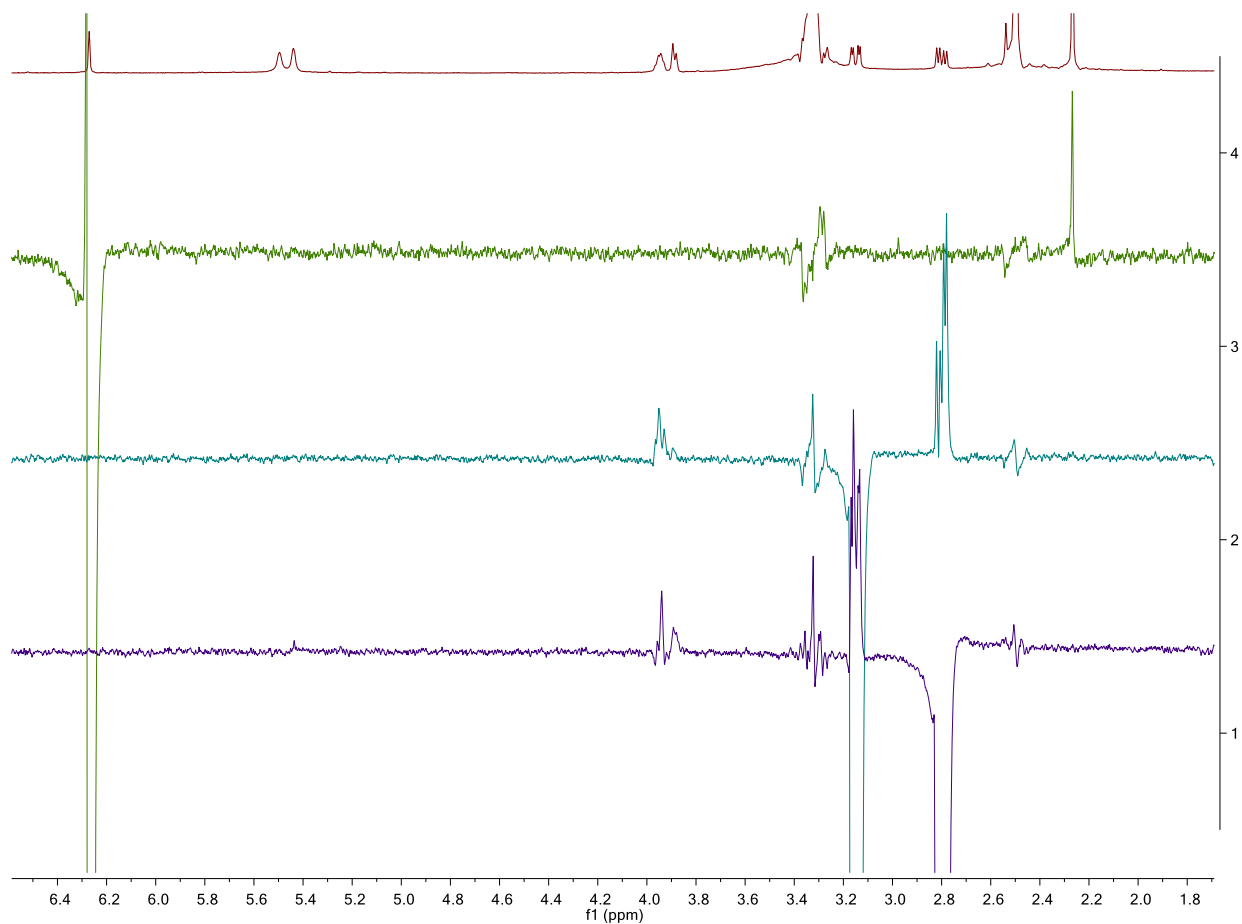


Figure S39. 1D NOESY Spectrum of **6** in DMSO- d_6

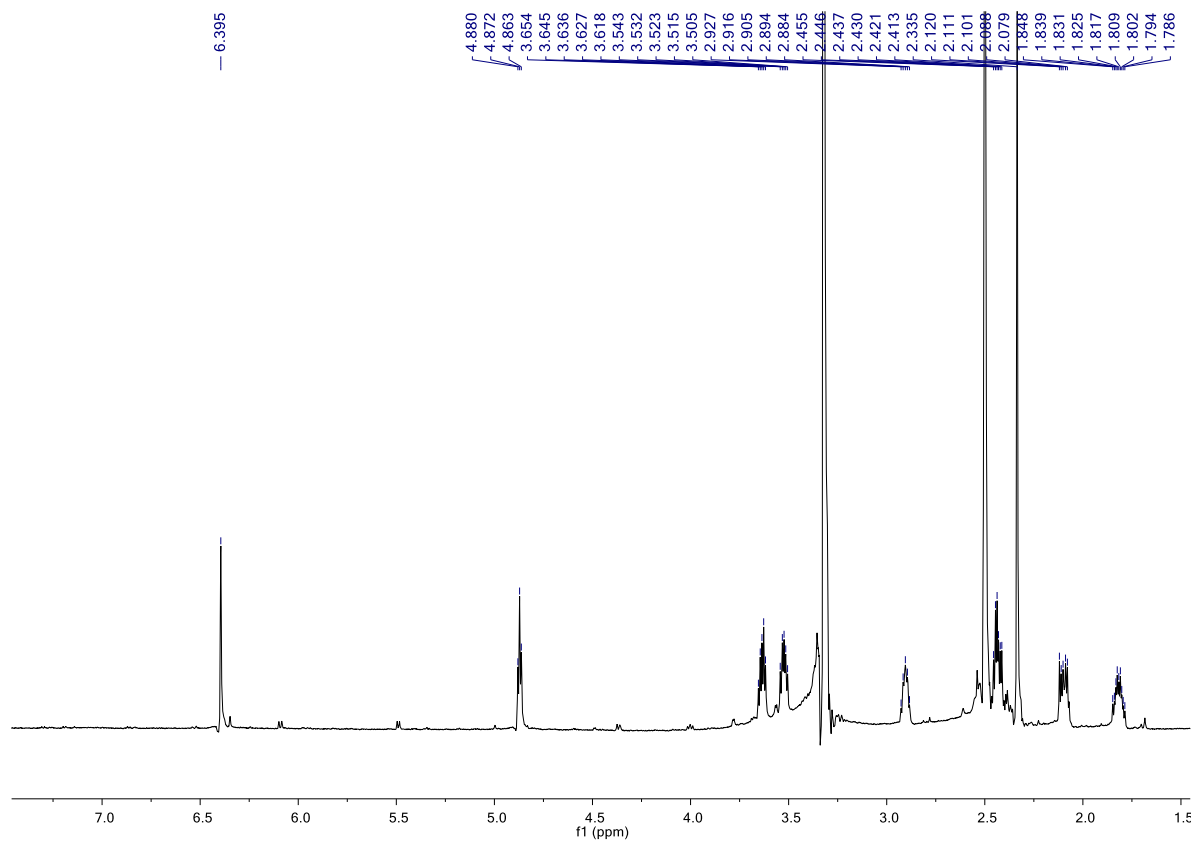


Figure S40. ^1H Spectrum of **7** in DMSO- d_6

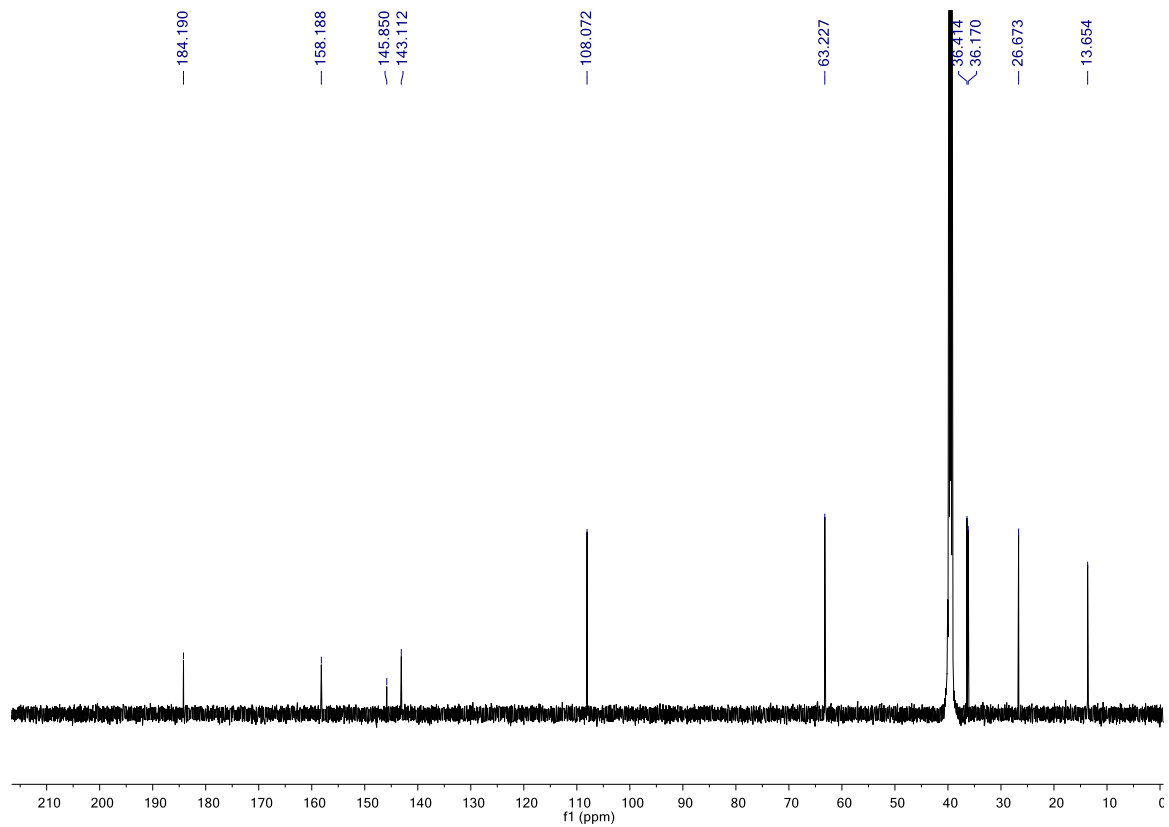


Figure S41. ^{13}C Spectrum of 7 in $\text{DMSO-}d_6$

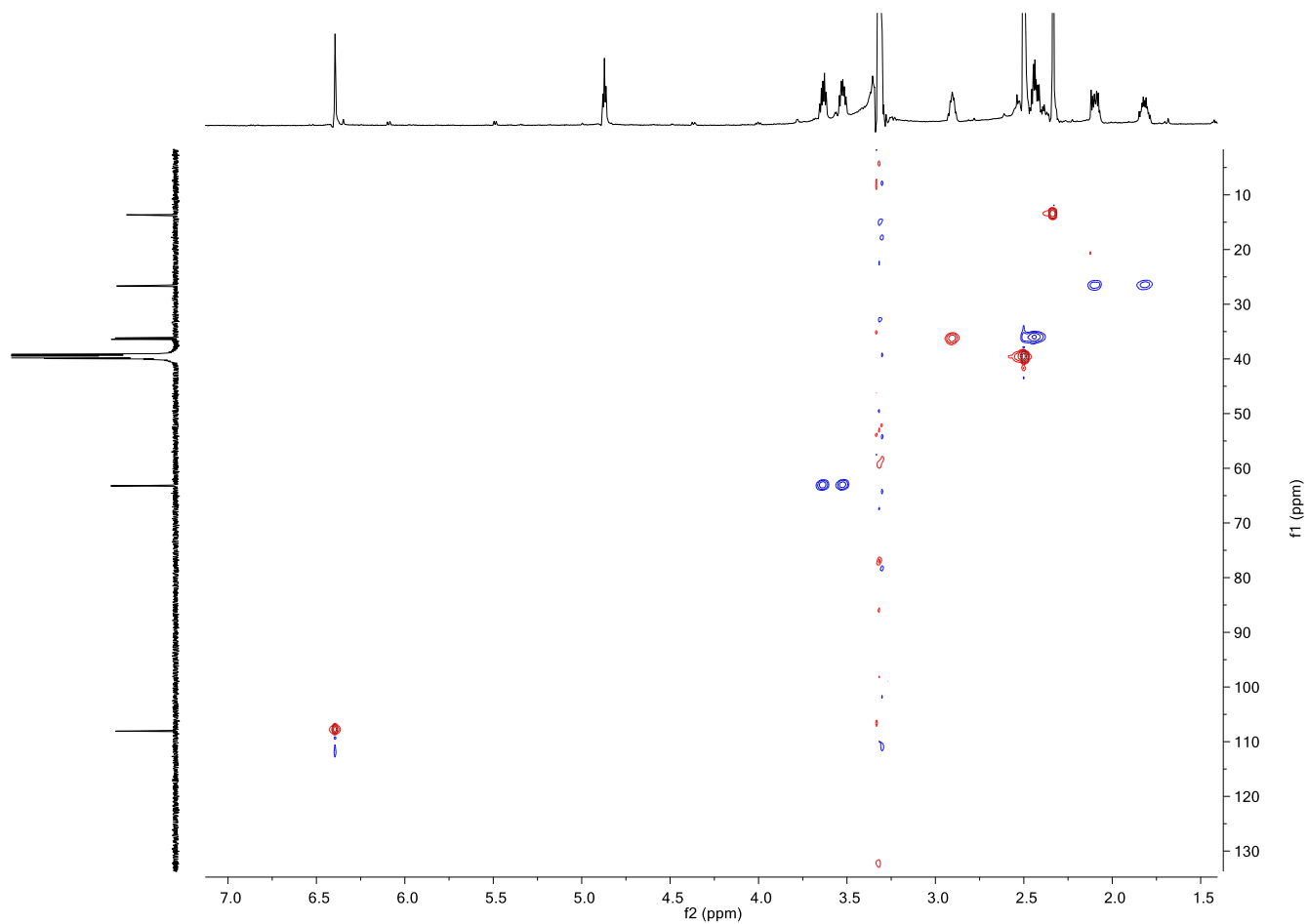


Figure S42. HSQC Spectrum of 7 in $\text{DMSO-}d_6$

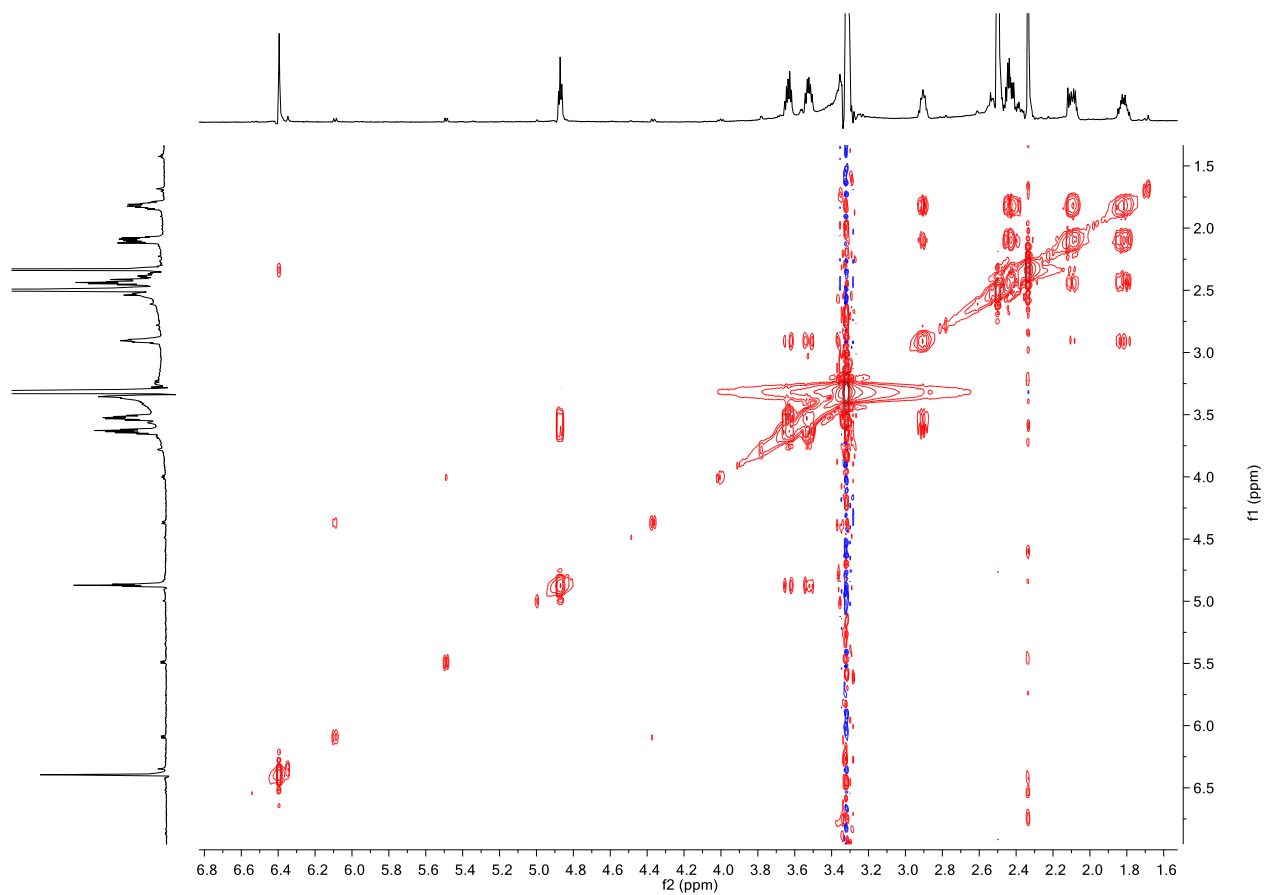


Figure S43. COSY Spectrum of **7** in DMSO- d_6

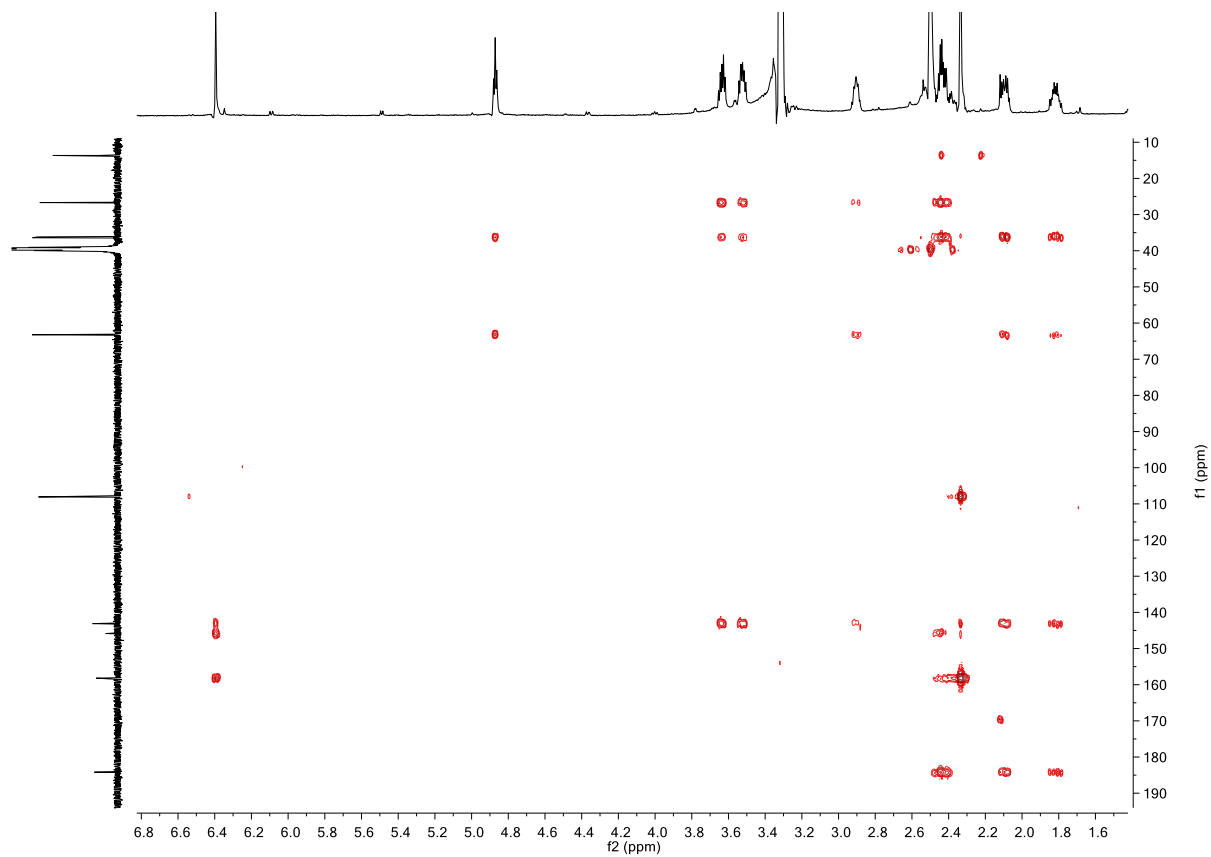


Figure S44. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **7** in DMSO- d_6

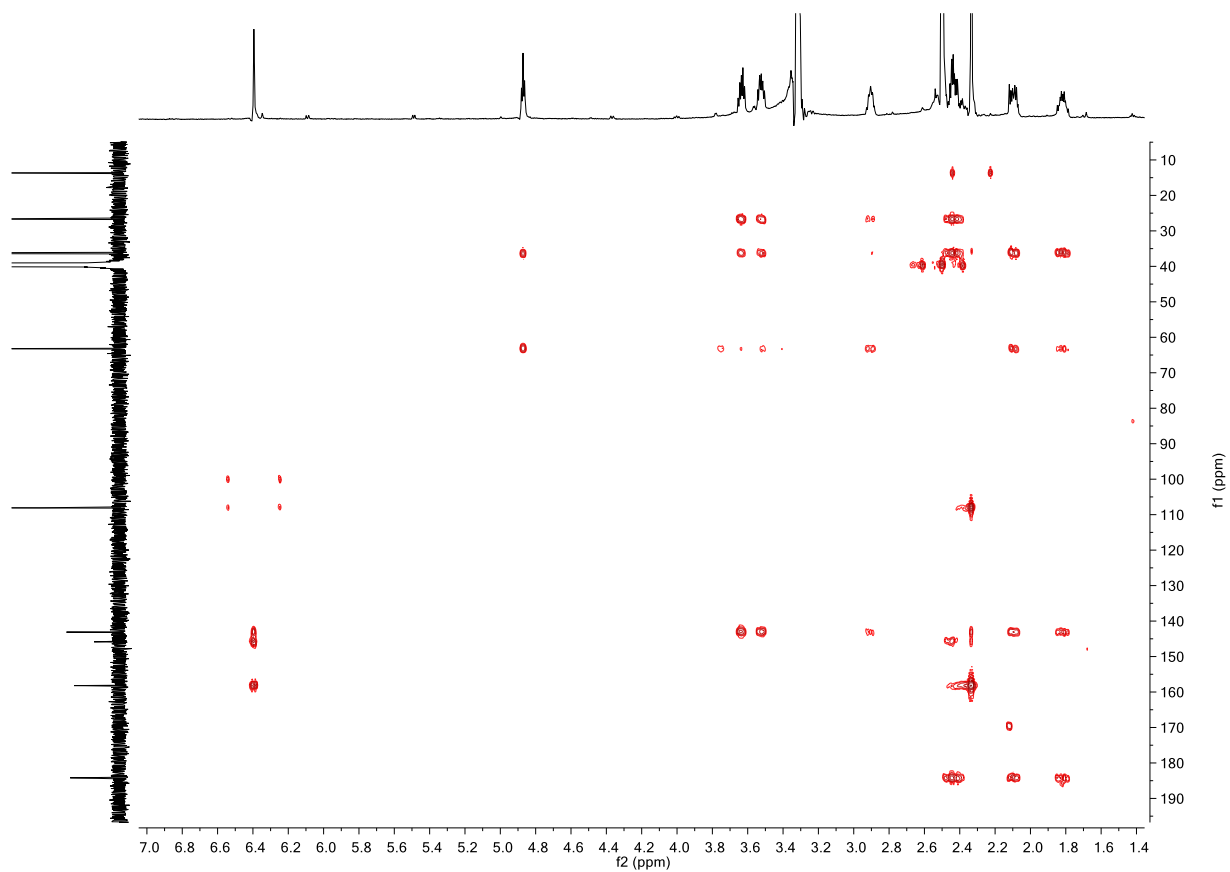


Figure S45. HMBC ($J_{\text{HC}} = 3 \text{ Hz}$) Spectrum of **7** in DMSO-*d*₆

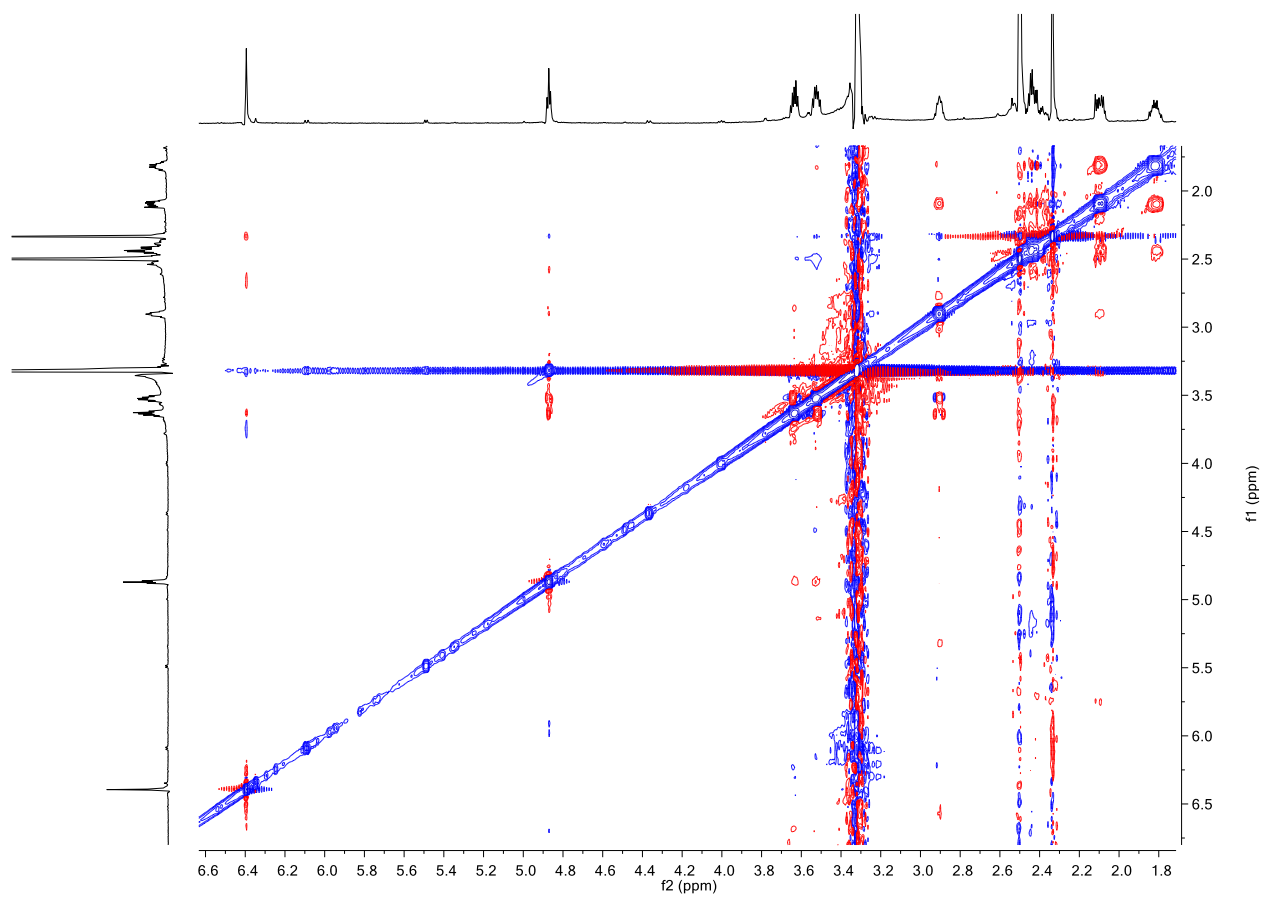


Figure S46. 2D ROESY Spectrum of **7** in DMSO-*d*₆

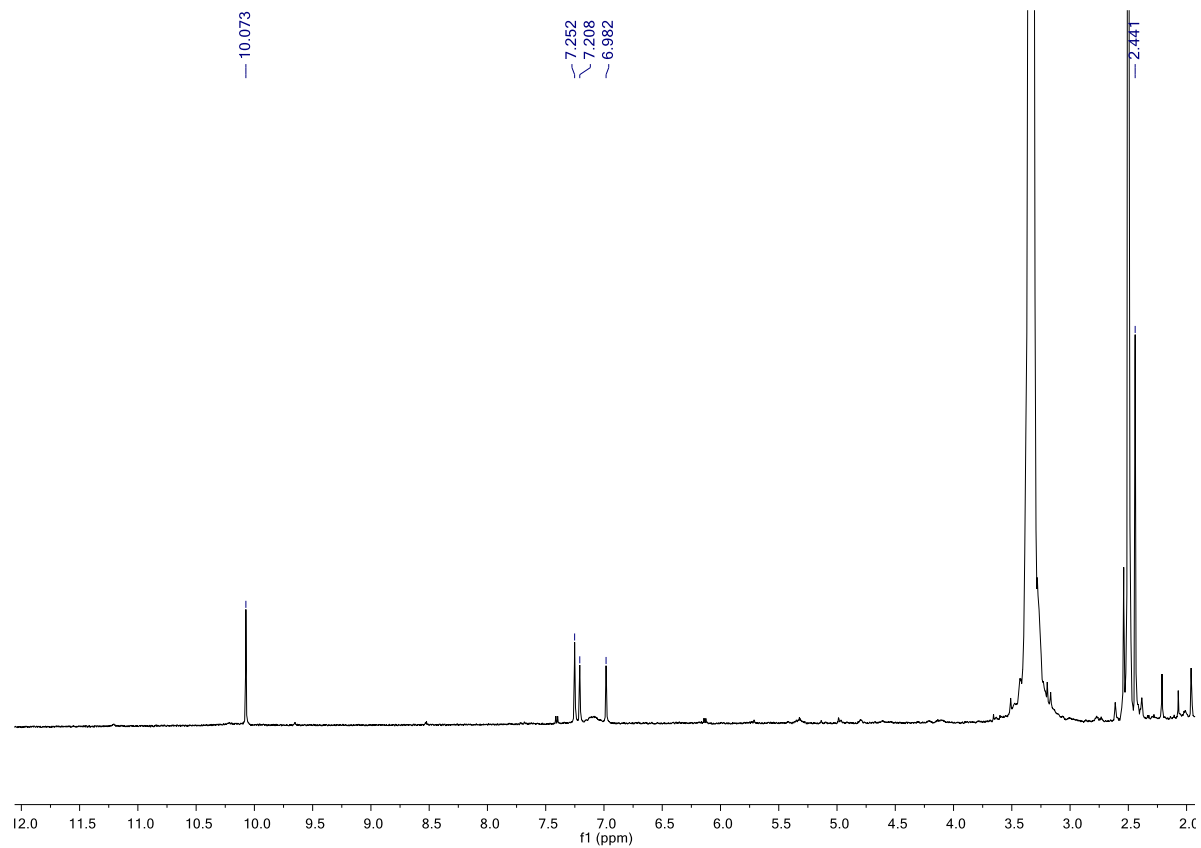


Figure S47. ^1H Spectrum of **8** in $\text{DMSO-}d_6$

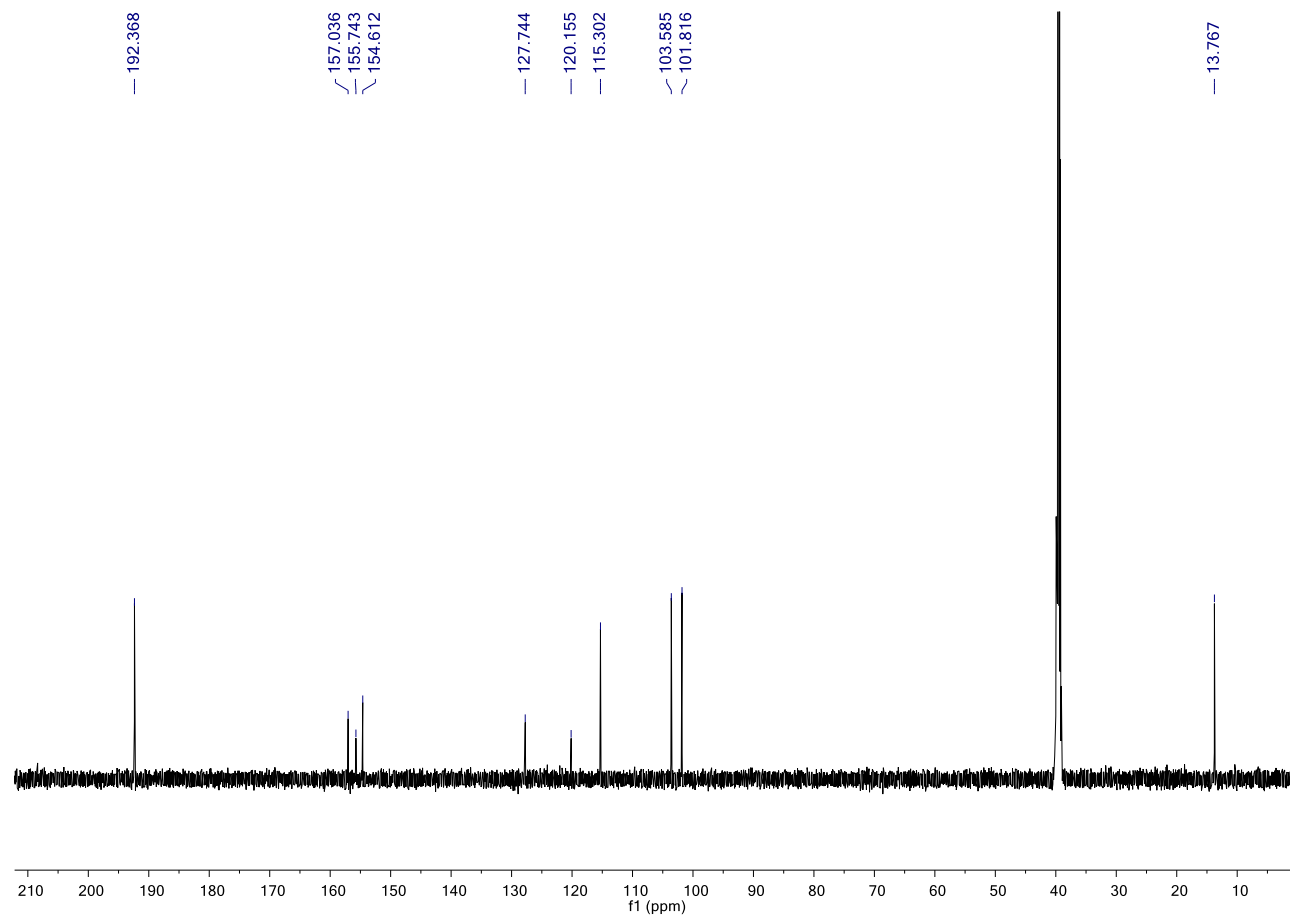


Figure S48. ^{13}C Spectrum of **8** in $\text{DMSO-}d_6$

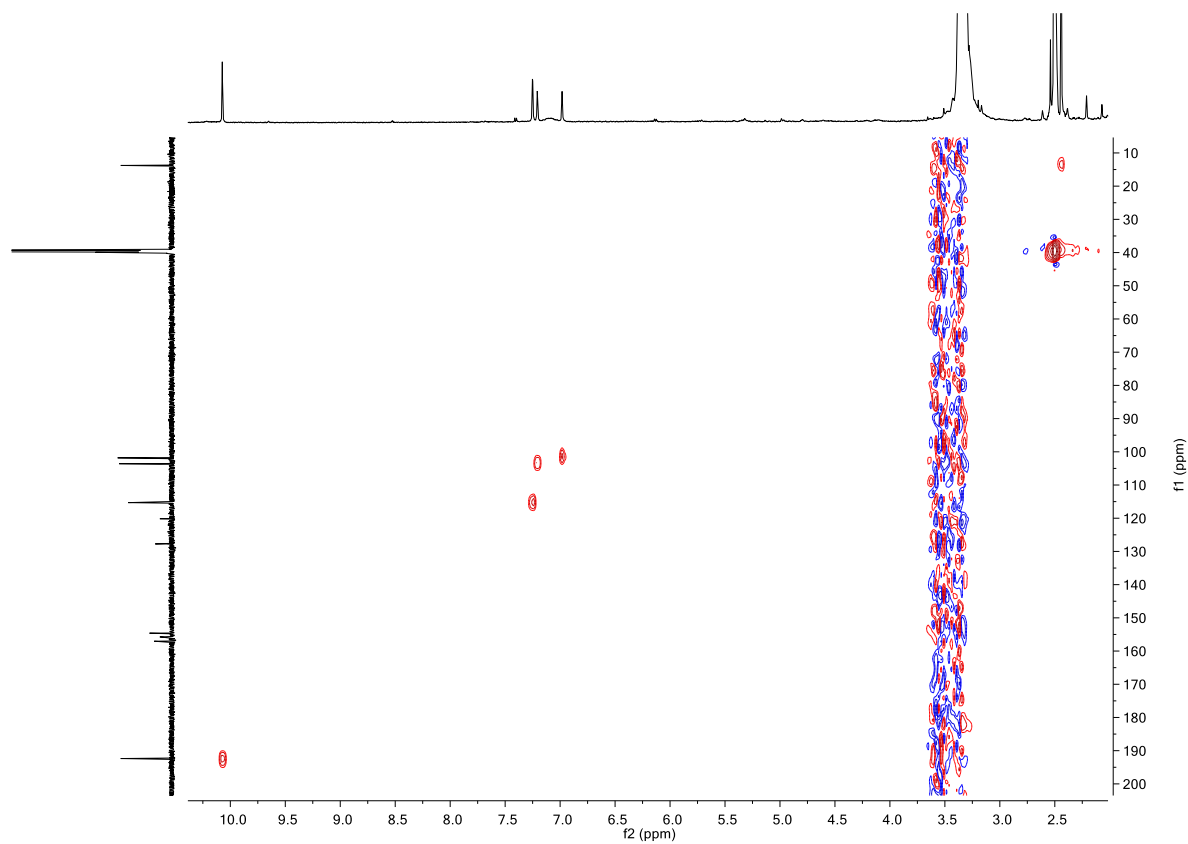


Figure S49. HSQC Spectrum of **8** in DMSO- d_6

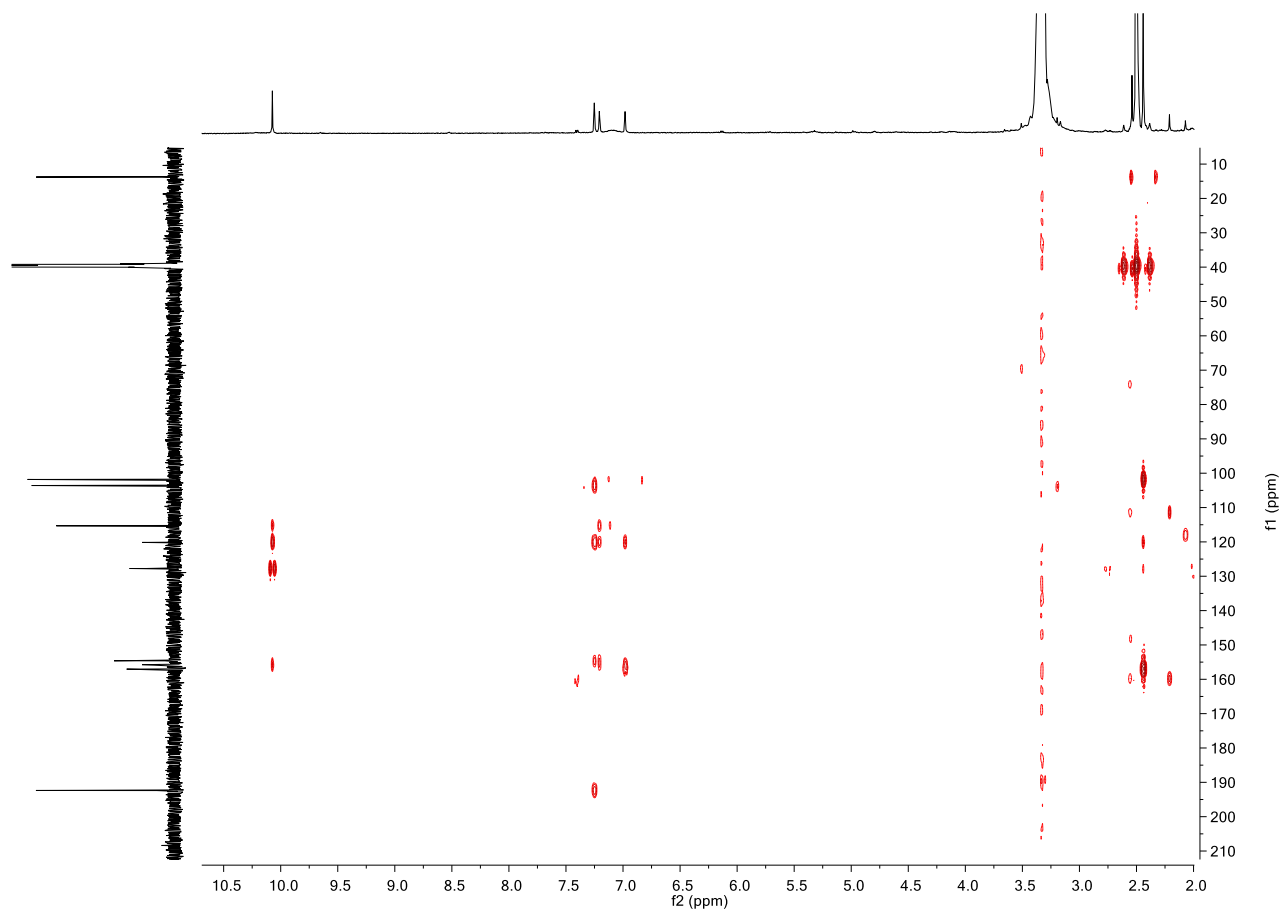


Figure S50. HMBC ($J_{\text{HC}} = 8$ Hz) Spectrum of **8** in DMSO- d_6

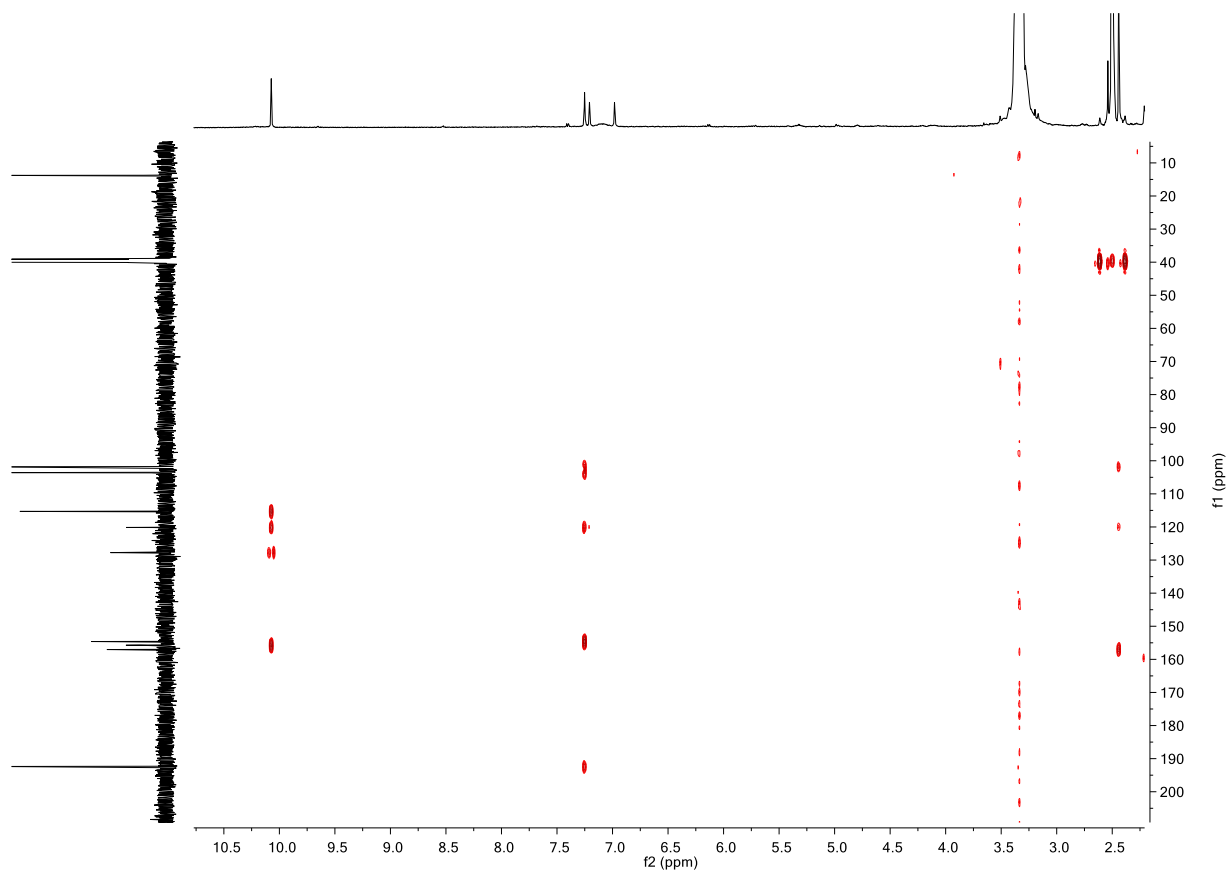


Figure S51. HMBC ($J_{\text{HC}} = 2 \text{ Hz}$) Spectrum of **8** in DMSO- d_6

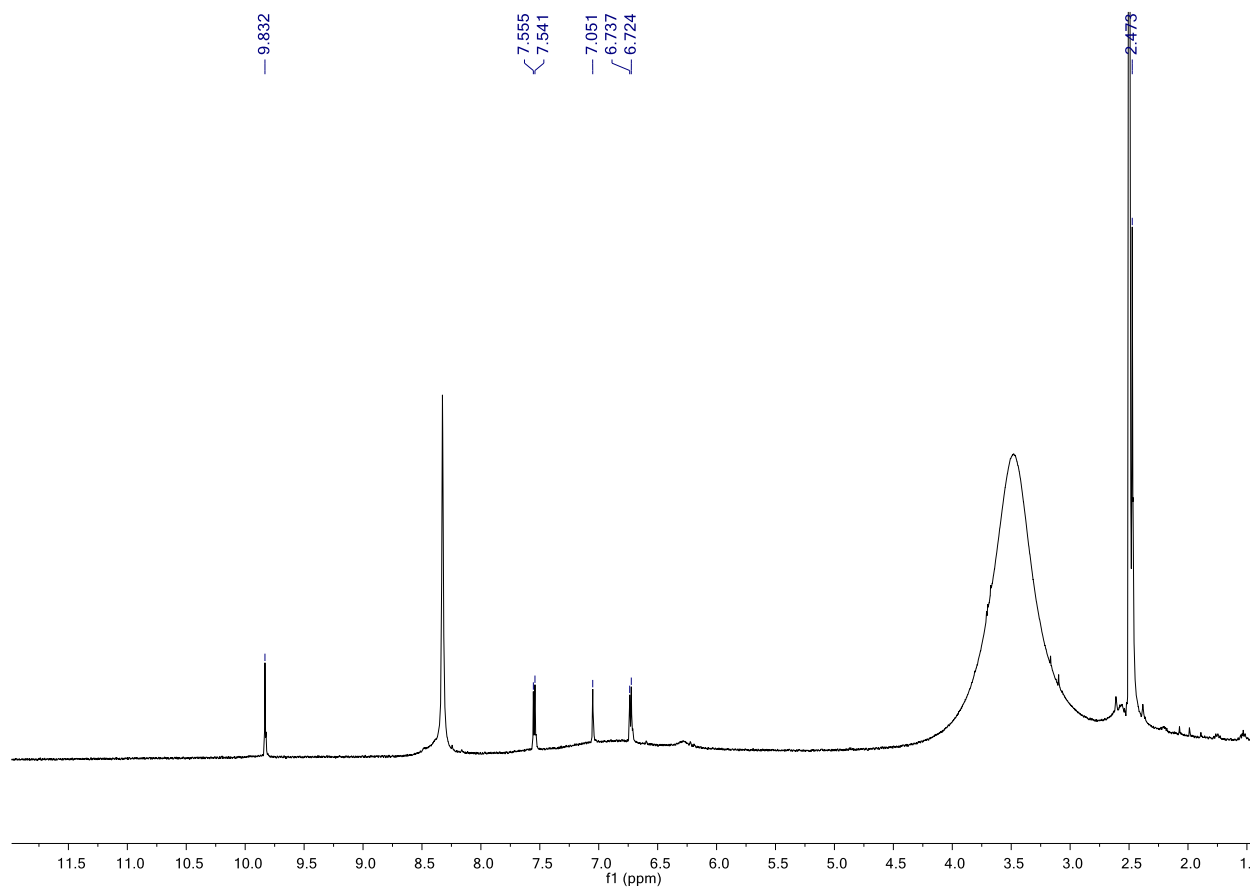


Figure S52. ^1H Spectrum of **9** in DMSO- d_6

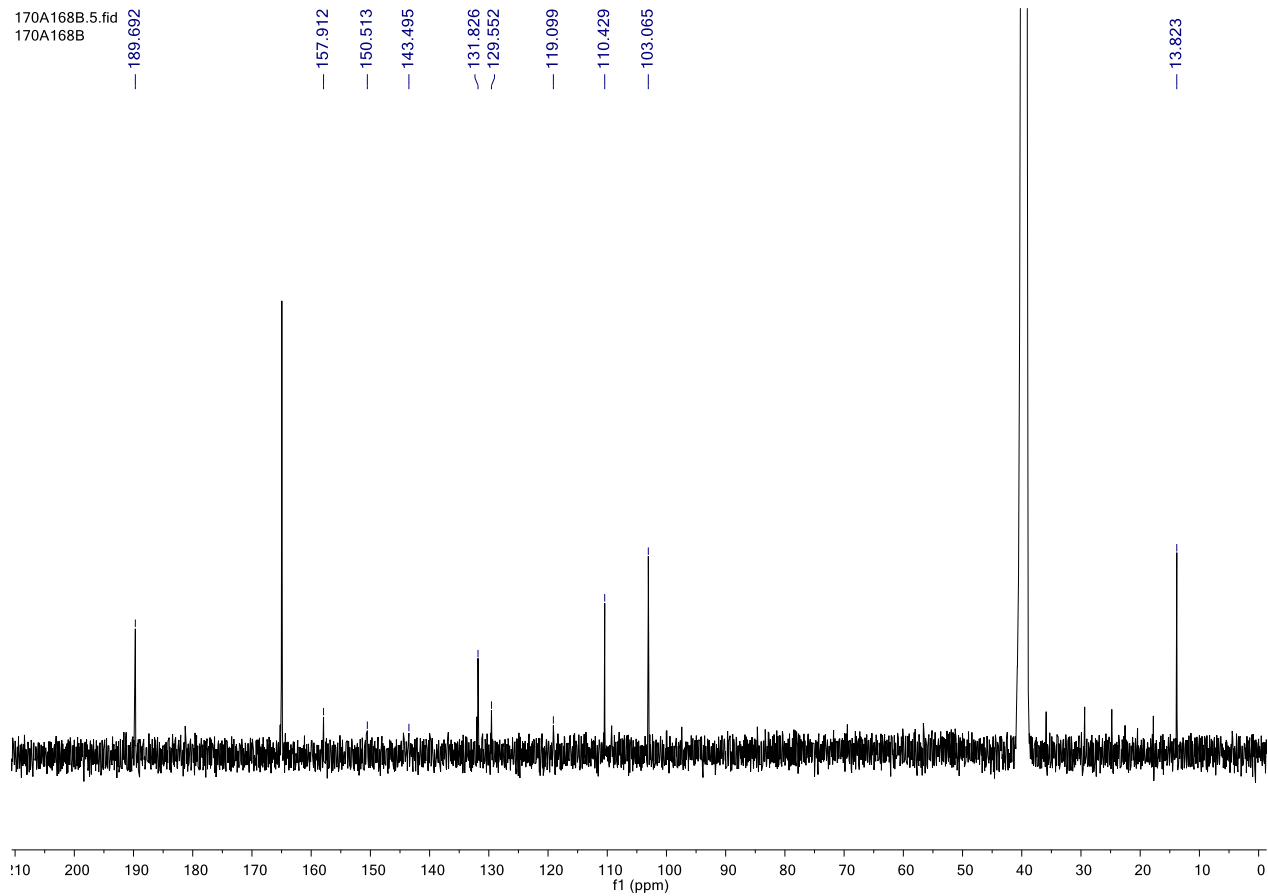


Figure S53. ^{13}C Spectrum of **9** in $\text{DMSO-}d_6$

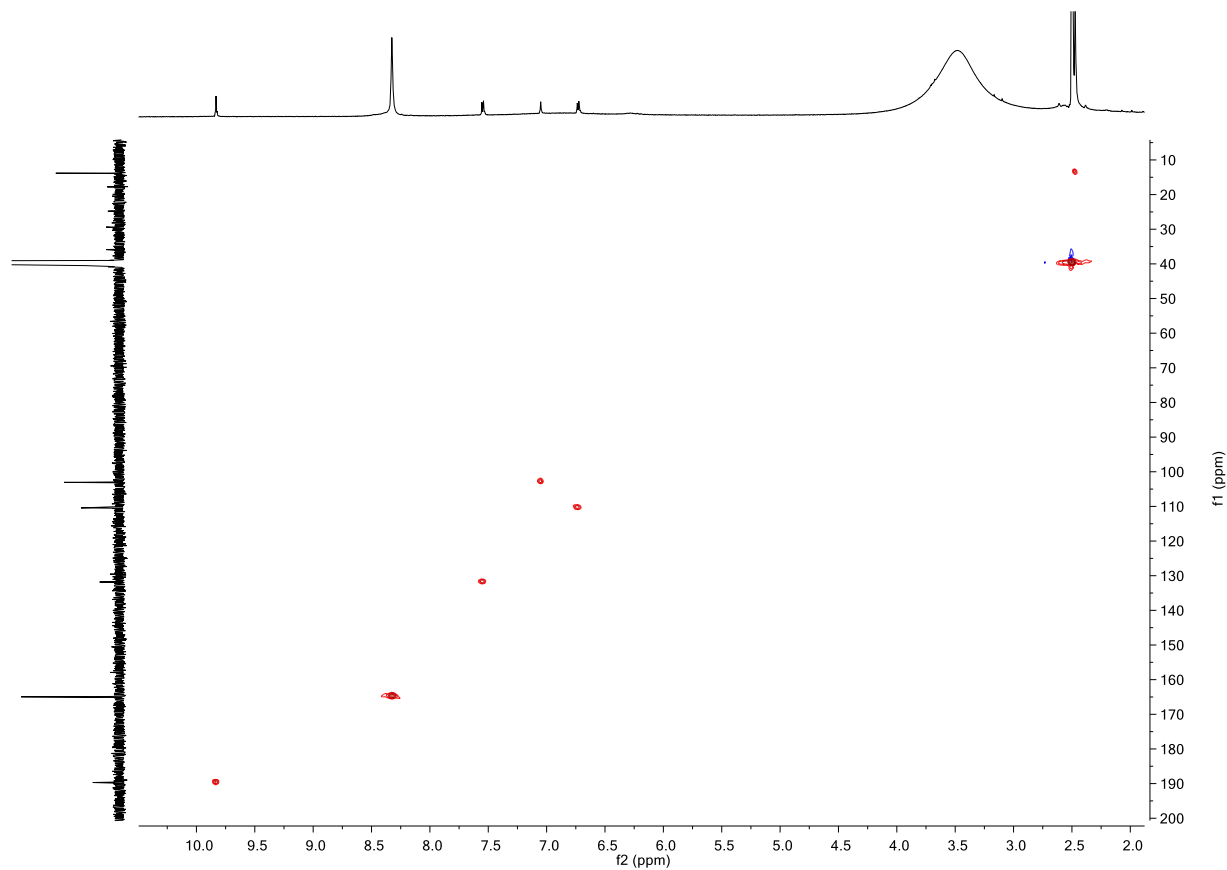


Figure S54. HSQC Spectrum of **9** in $\text{DMSO-}d_6$

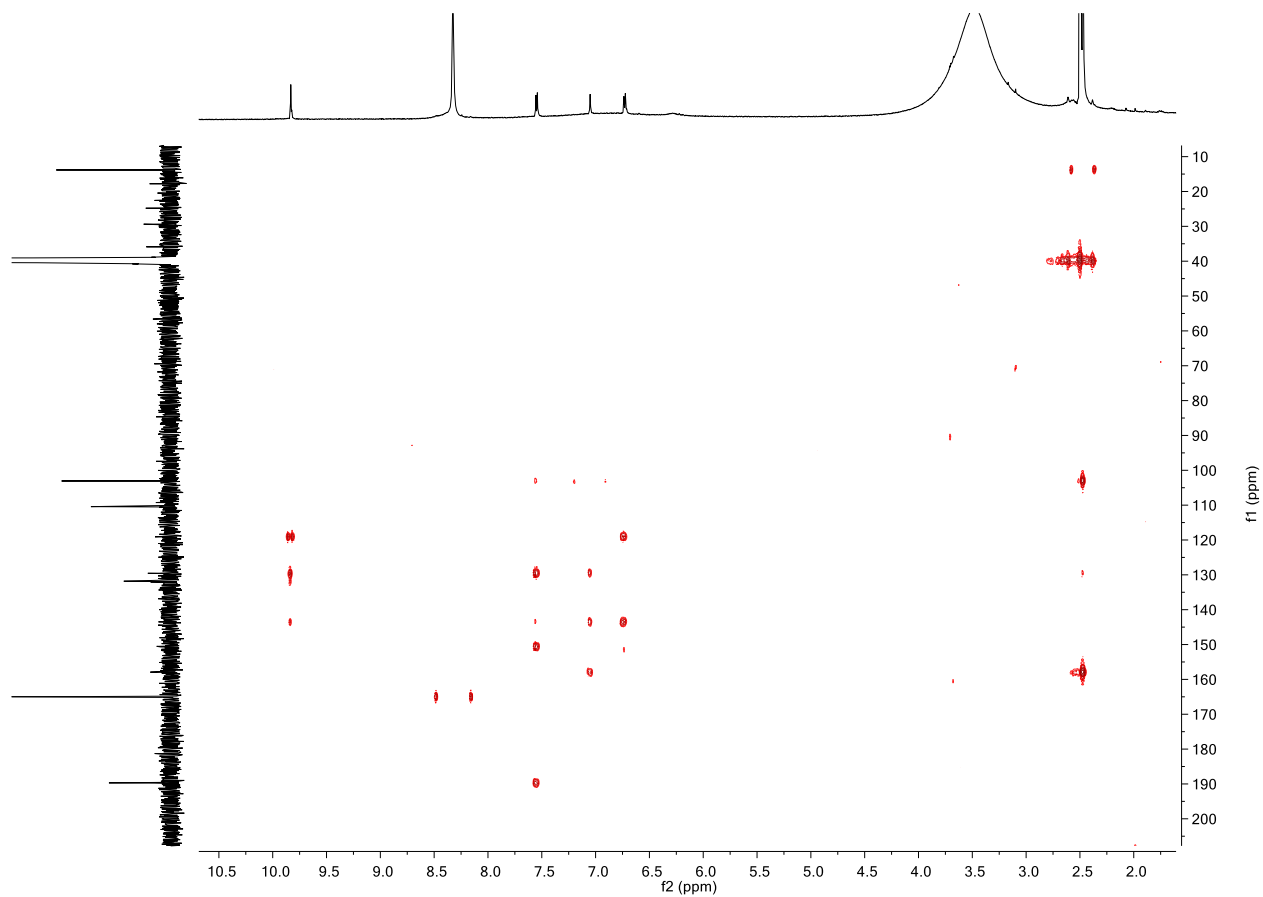


Figure S55. HMBC Spectrum of **9** in DMSO- d_6

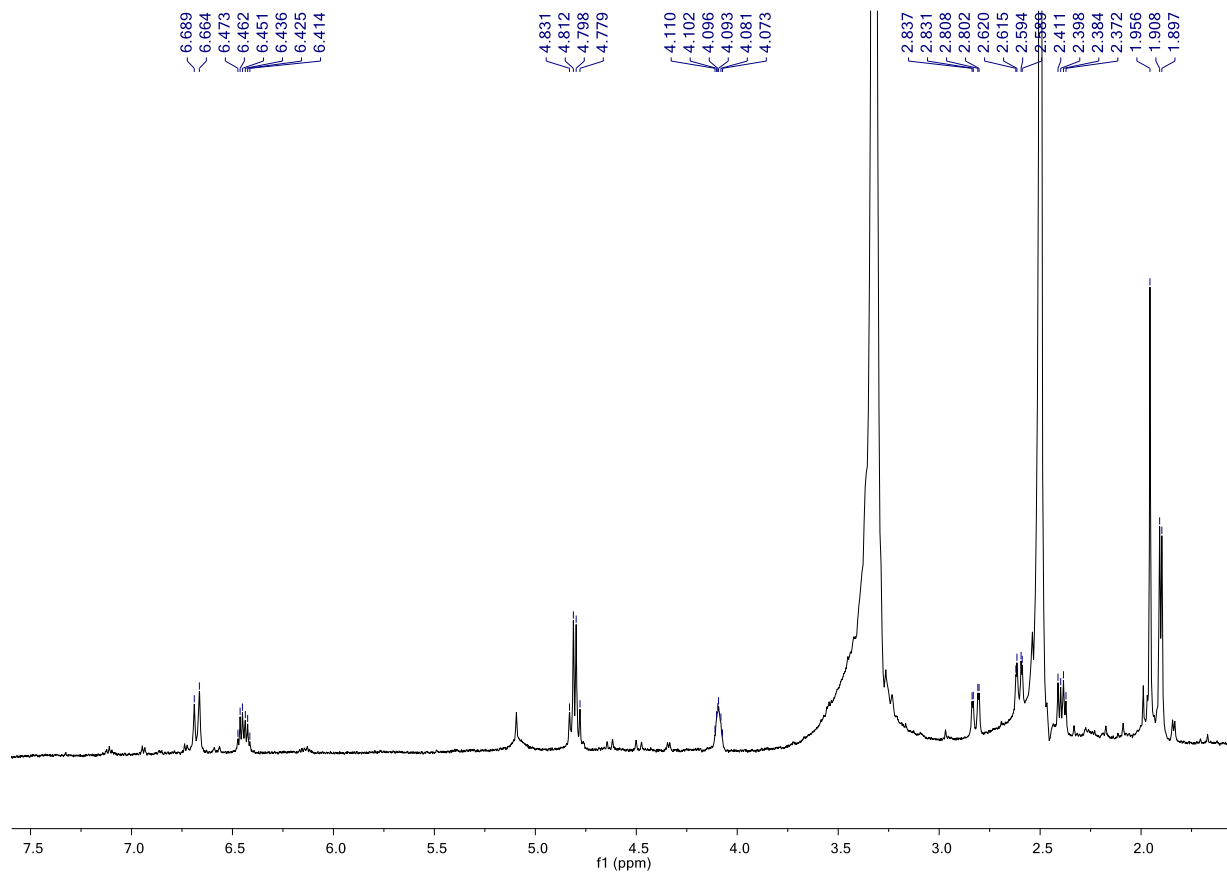


Figure S56. ^1H Spectrum of **10** in DMSO- d_6

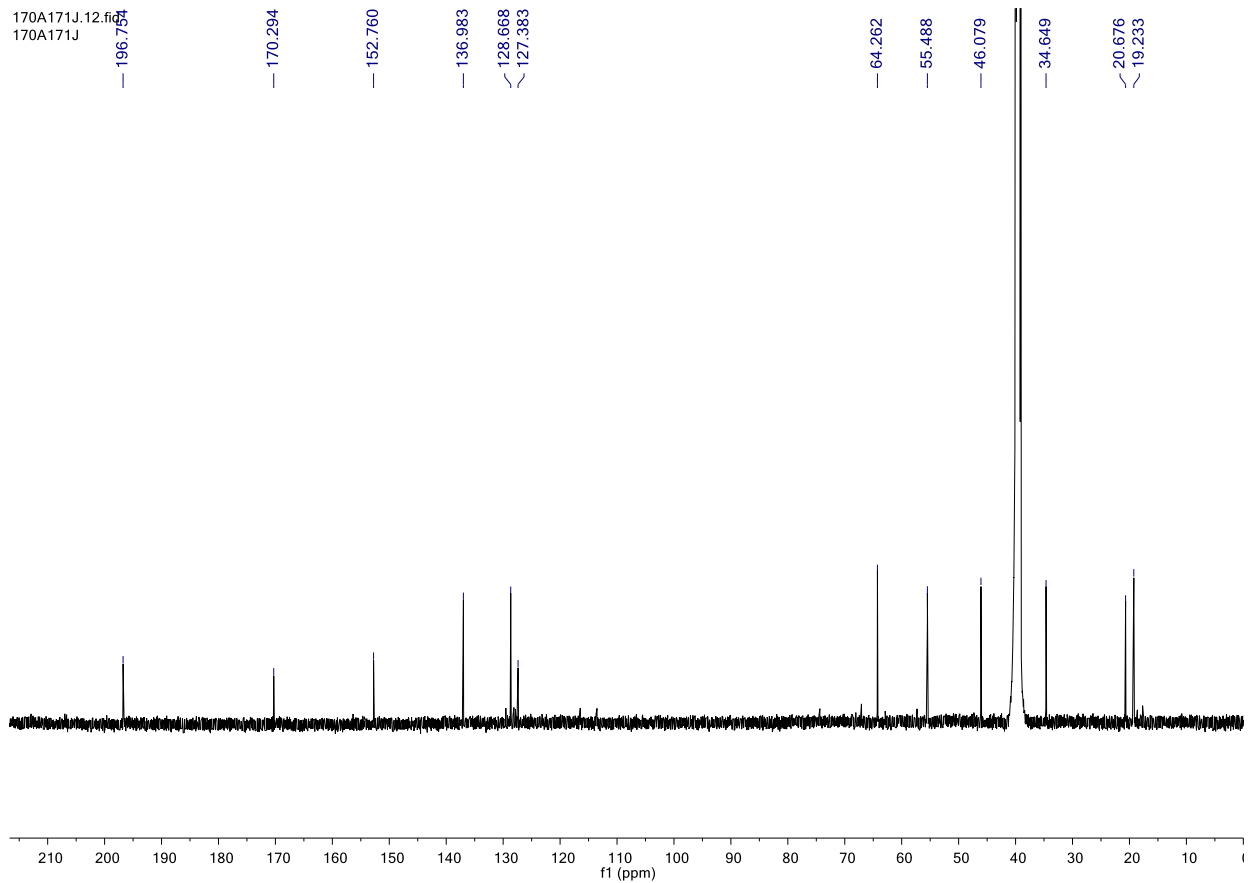


Figure S57. ^{13}C Spectrum of **10** in $\text{DMSO-}d_6$

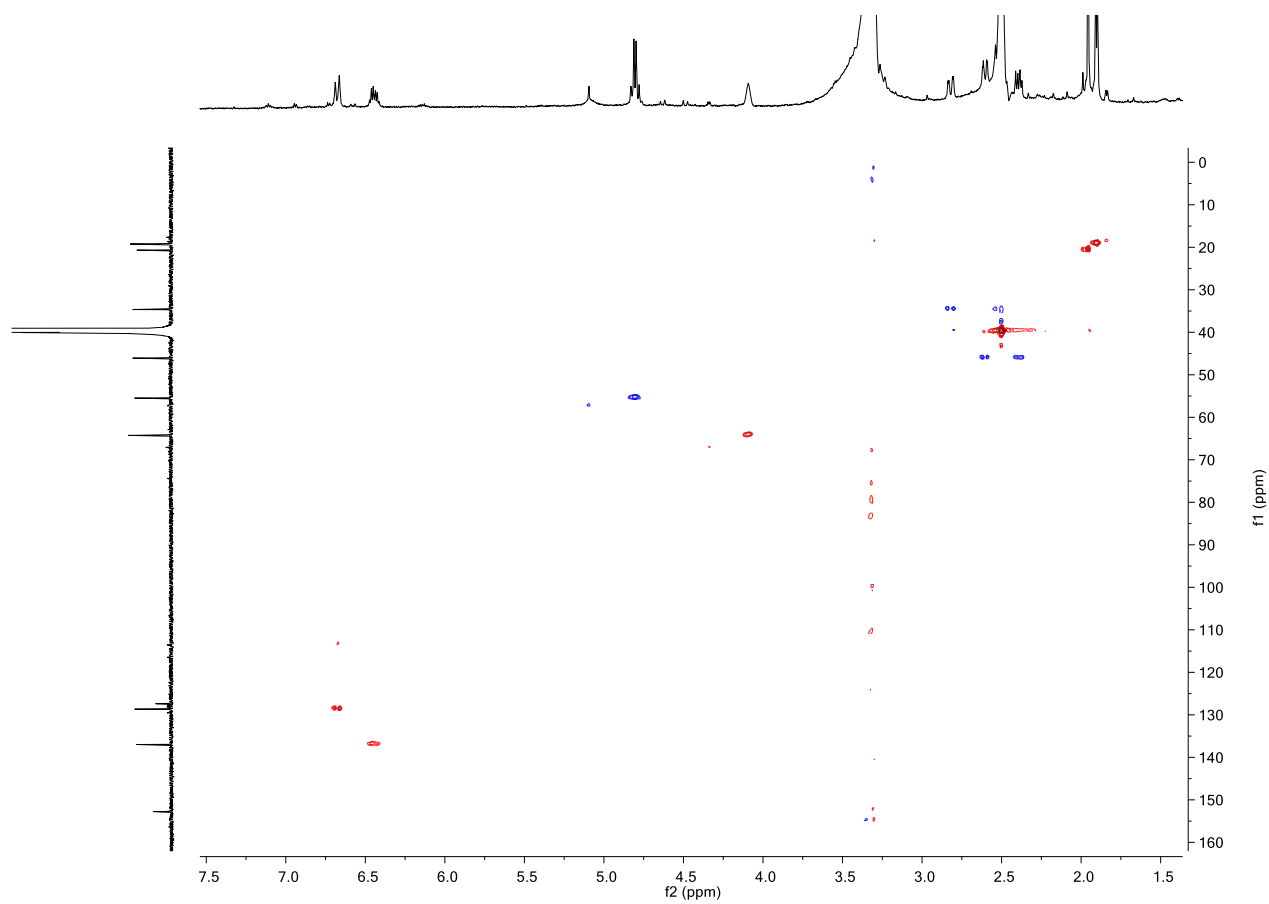


Figure S58. HSQC Spectrum of **10** in $\text{DMSO-}d_6$

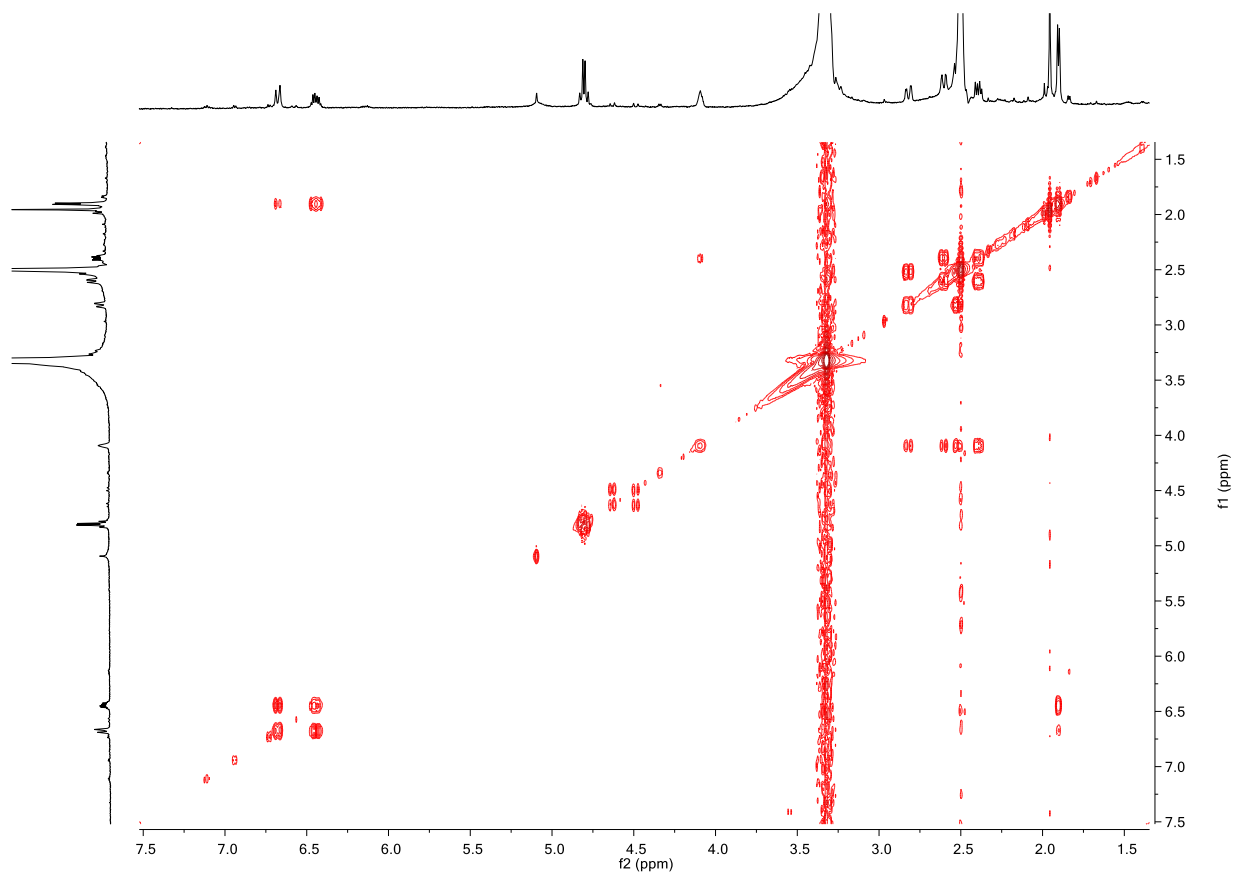


Figure S59. COSY Spectrum of **10** in DMSO- d_6

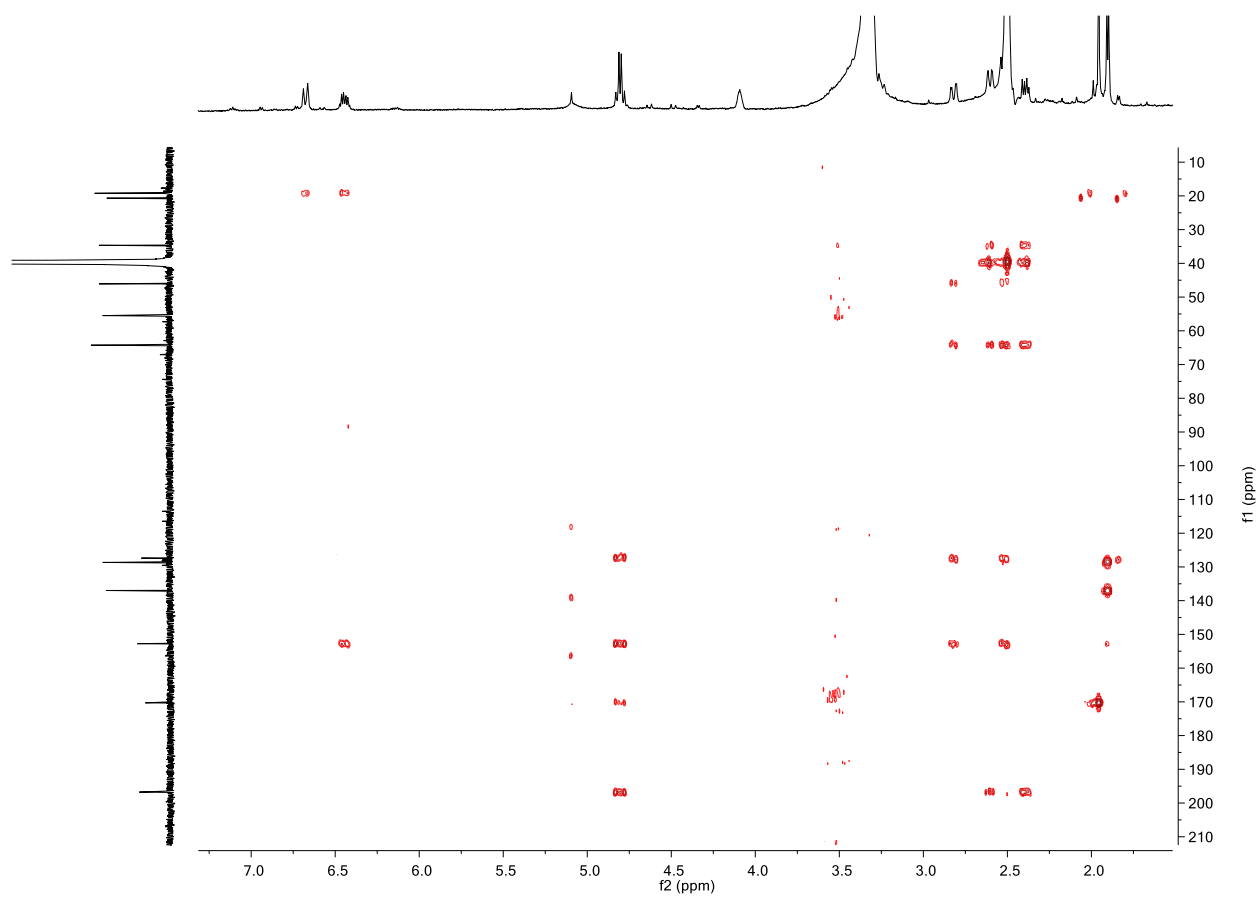


Figure S60. HMBC Spectrum of **10** in DMSO- d_6

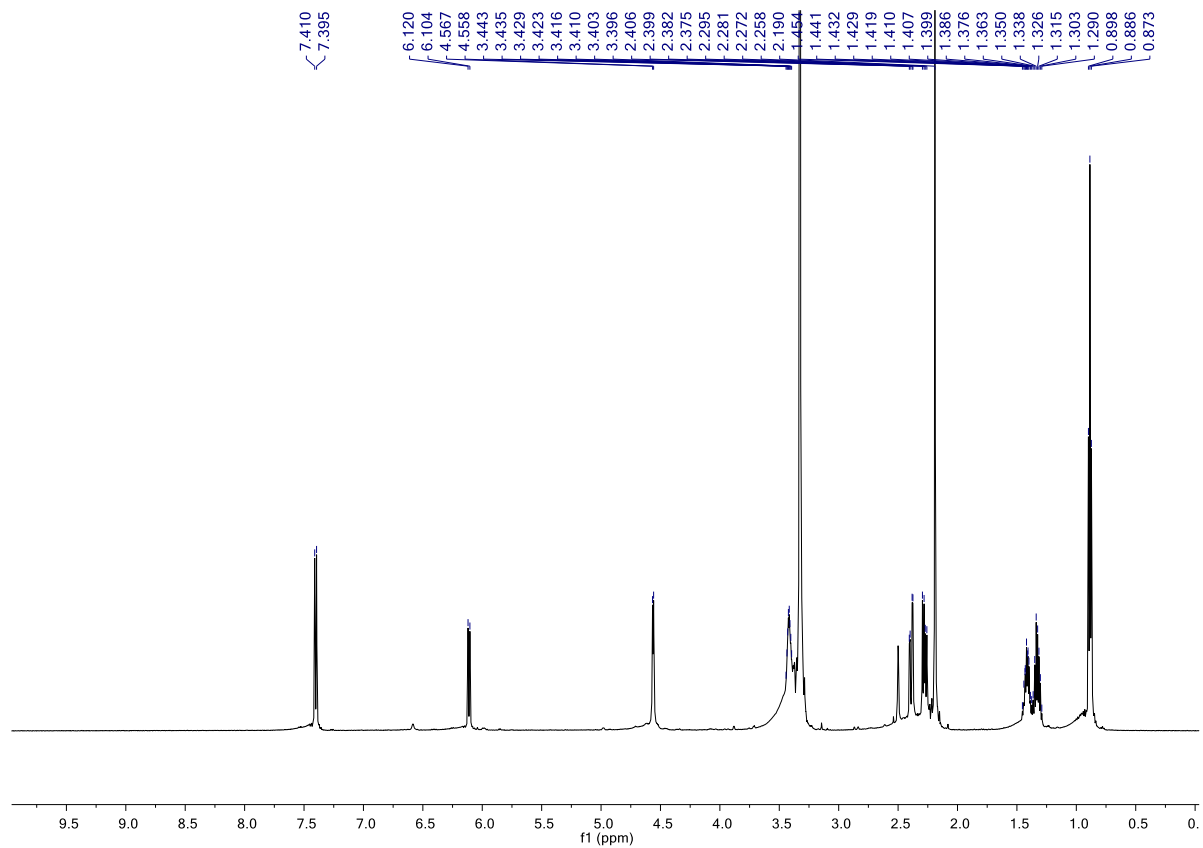


Figure S61. ^1H Spectrum of **11** in $\text{DMSO-}d_6$

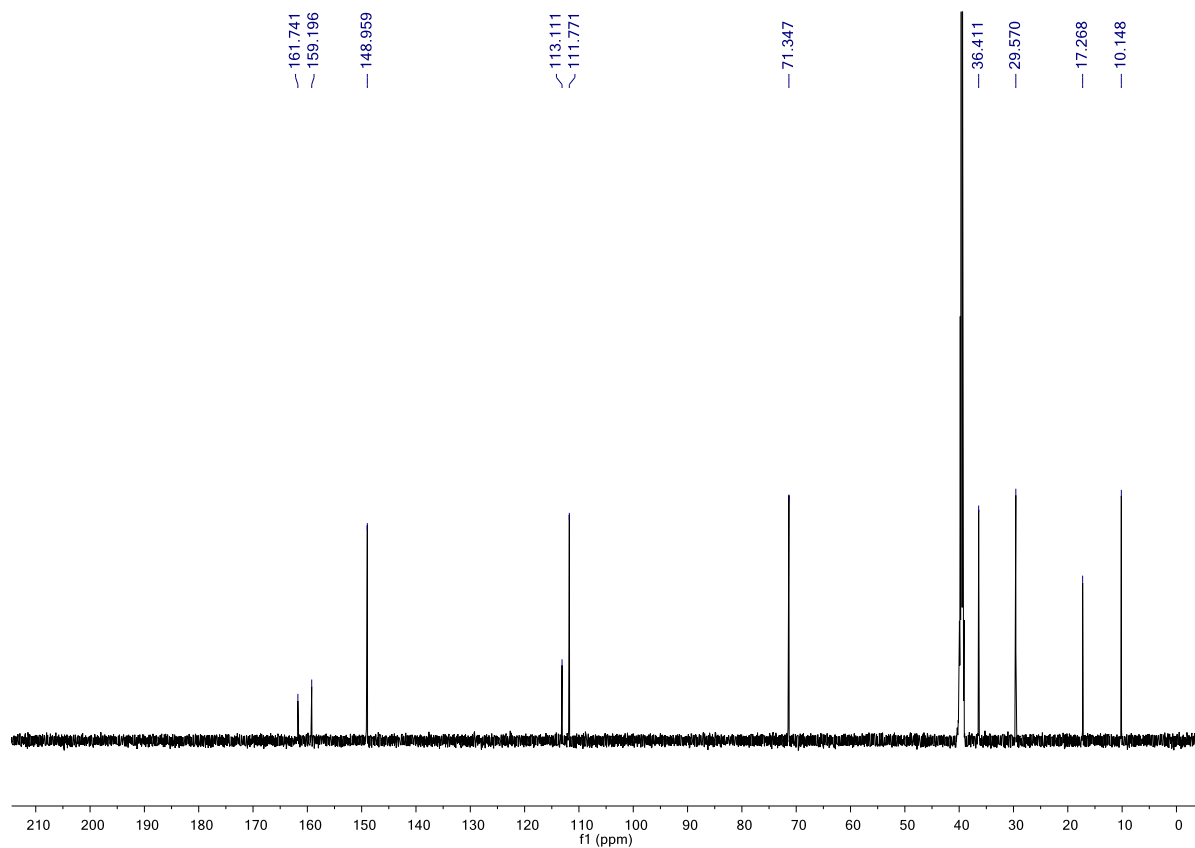


Figure S62. ^{13}C Spectrum of **11** in $\text{DMSO-}d_6$

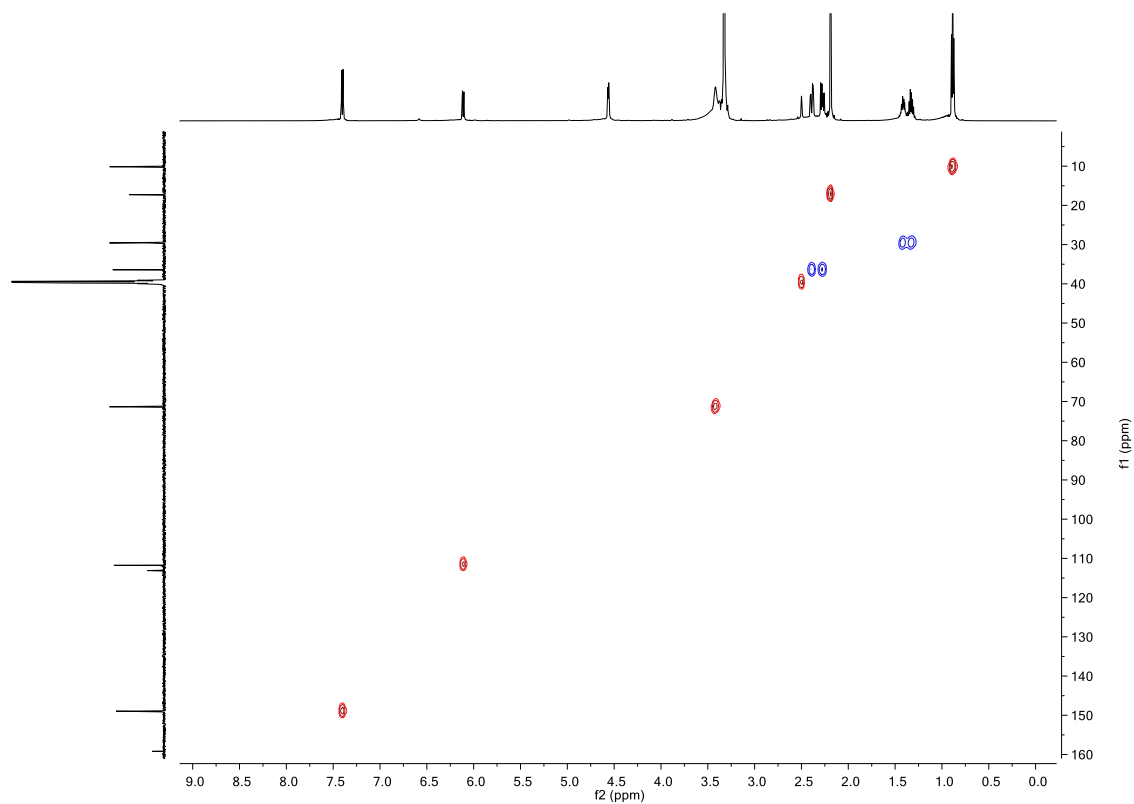


Figure S63. HSQC Spectrum of **11** in DMSO-*d*₆

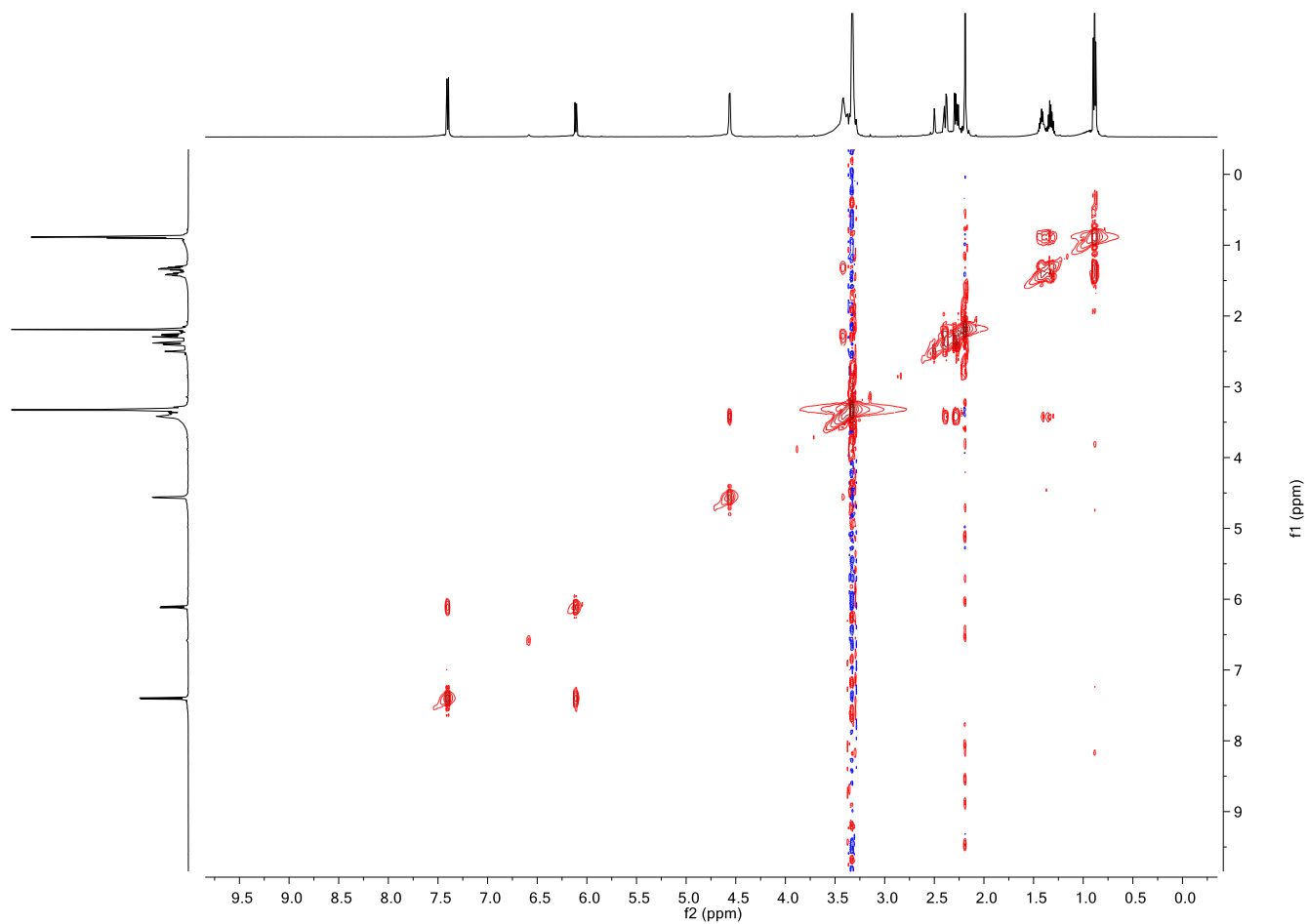


Figure S64. COSY Spectrum of **11** in DMSO-*d*₆

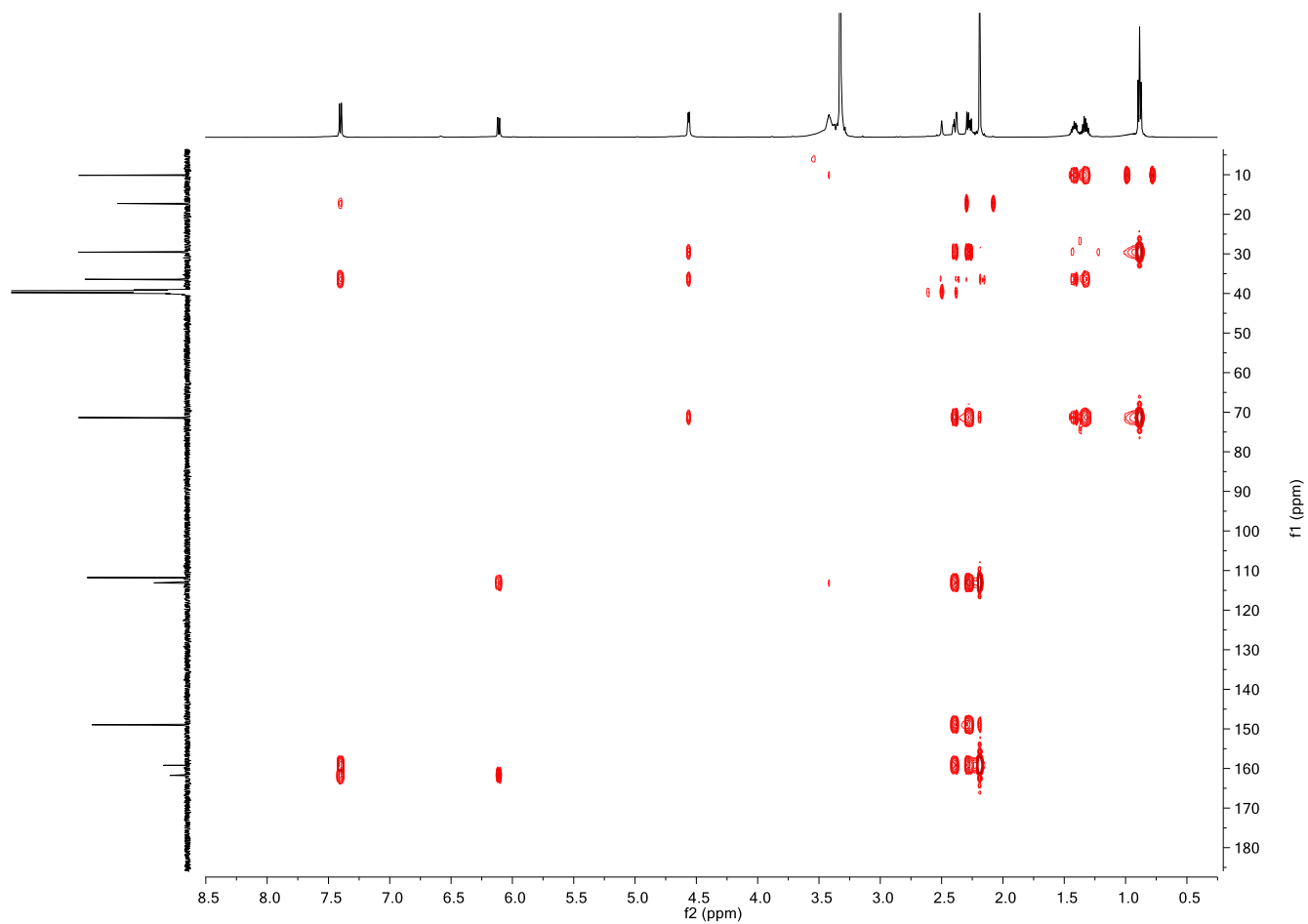


Figure S65. HMBC Spectrum of **11** in DMSO- d_6

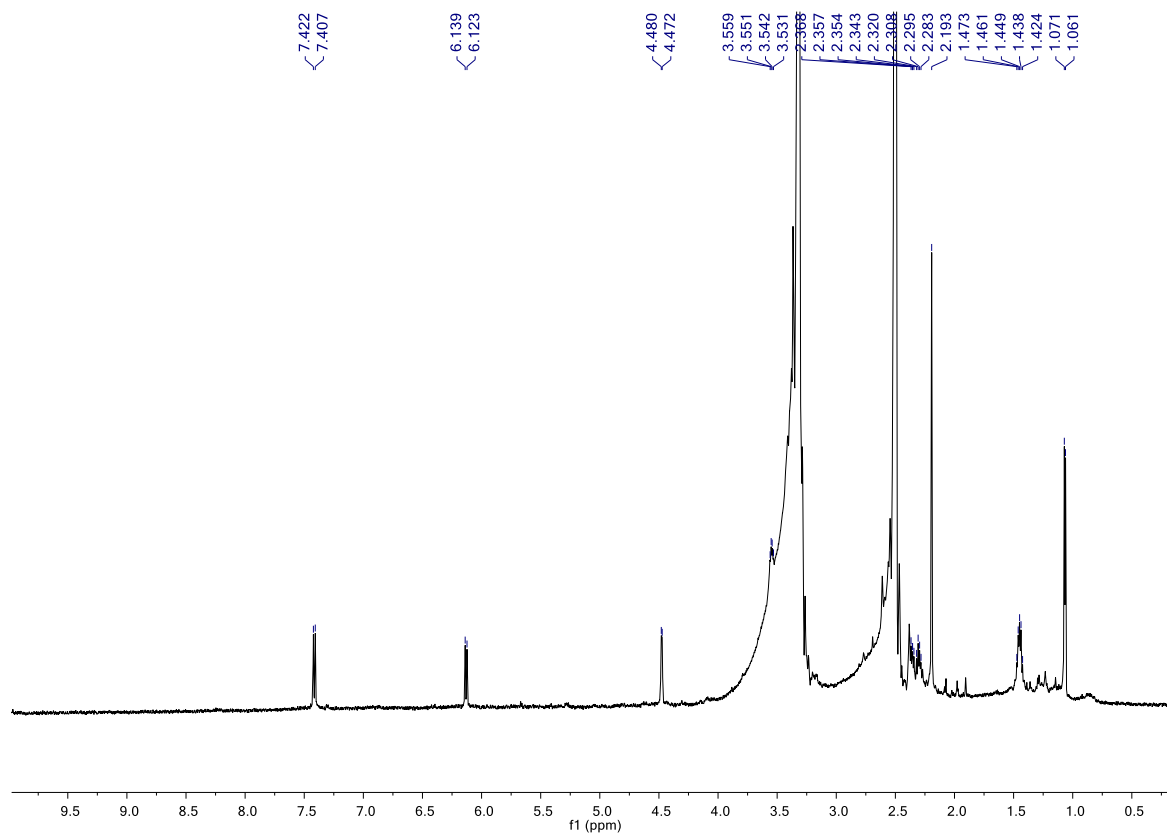


Figure S66. ^1H Spectrum of **12** in DMSO- d_6

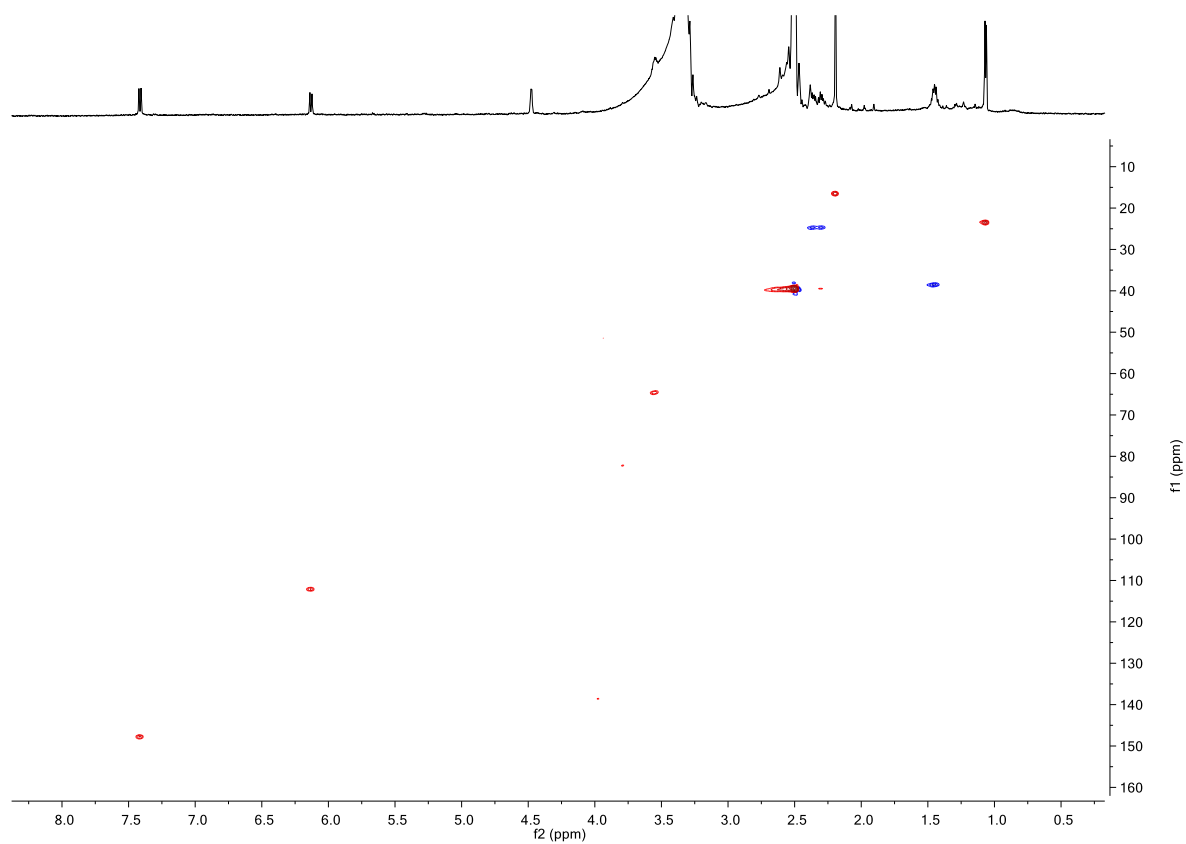


Figure S67. HSQC Spectrum of **12** in DMSO- d_6

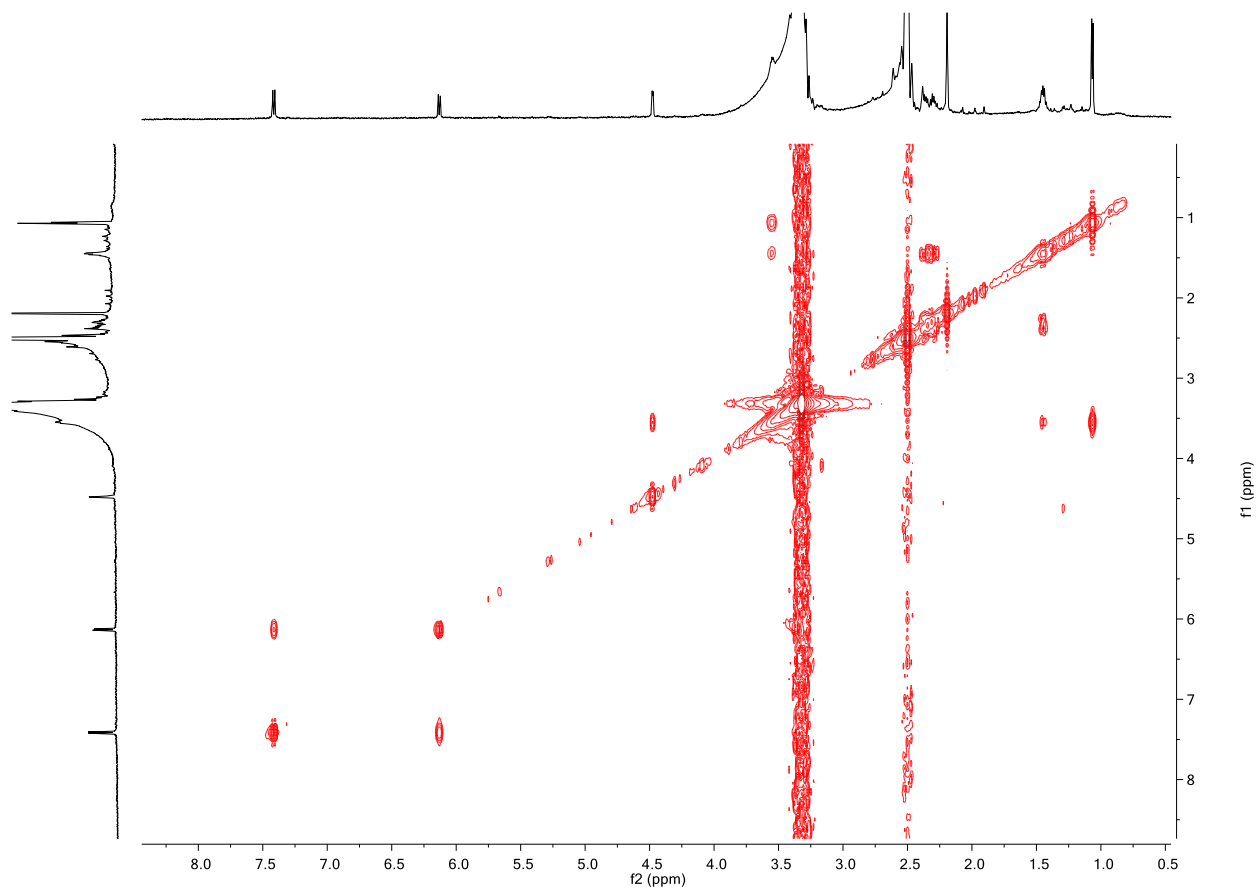


Figure S68. COSY Spectrum of **12** in DMSO- d_6

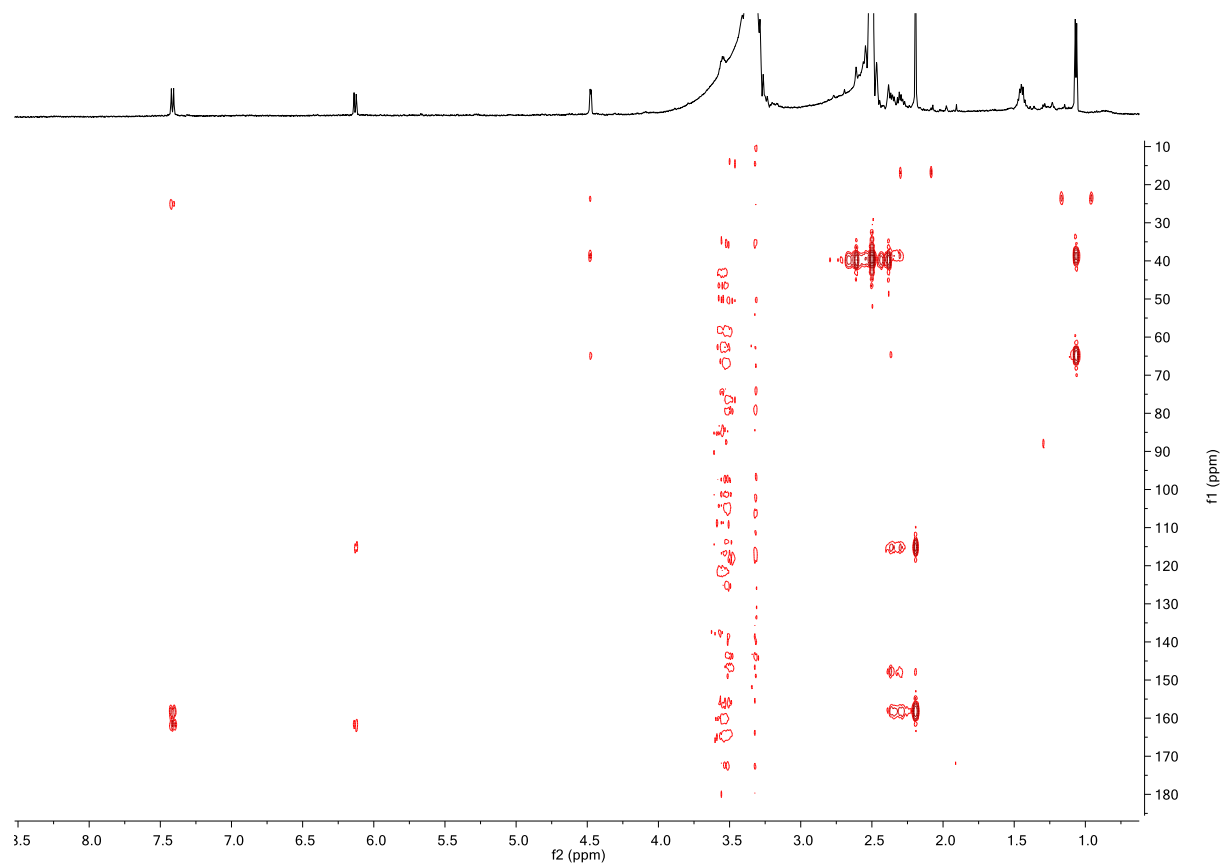


Figure S69. HMBC Spectrum of **12** in DMSO- d_6

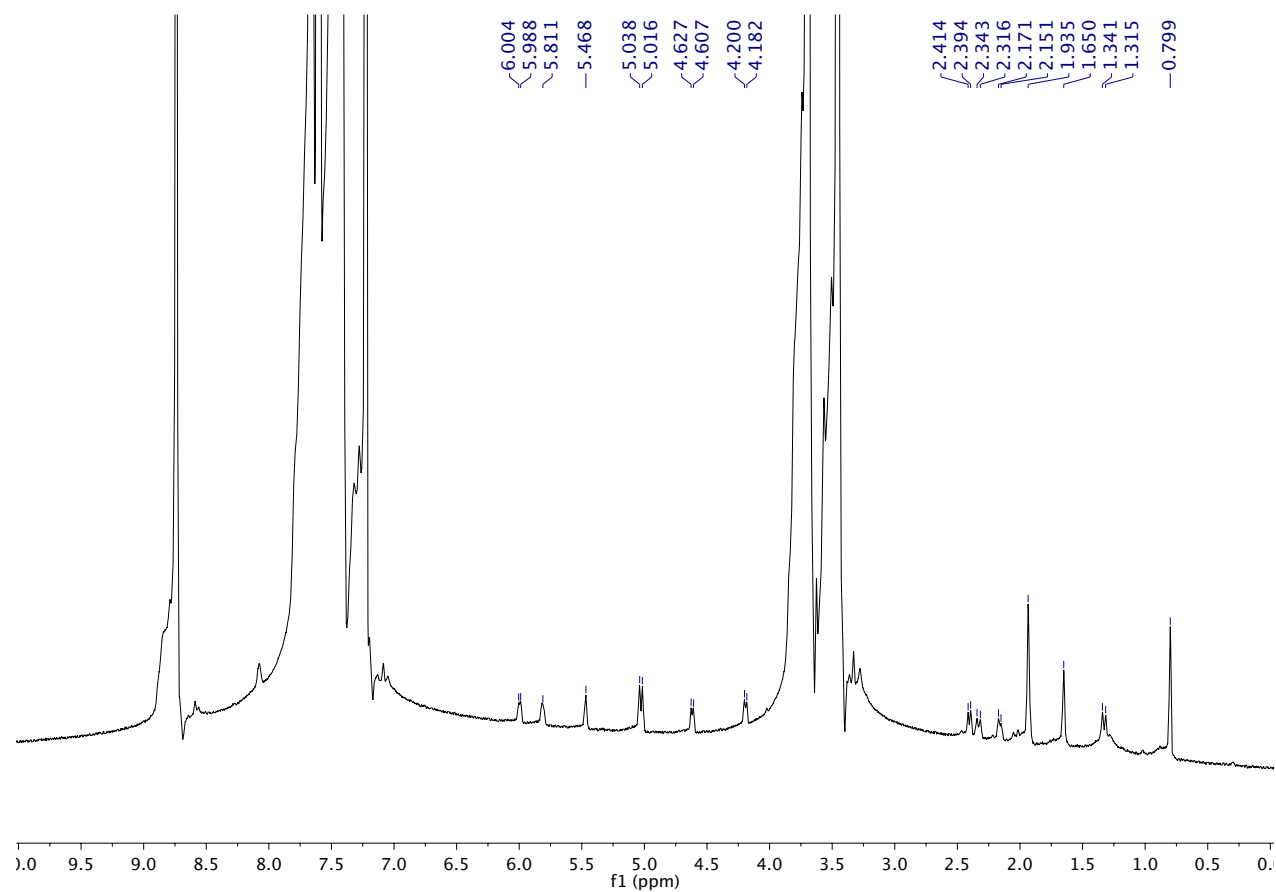


Figure S70. ^1H Spectrum of (*S*)-MTPA Ester of **1** (**1a**) in Pyridine- d_5

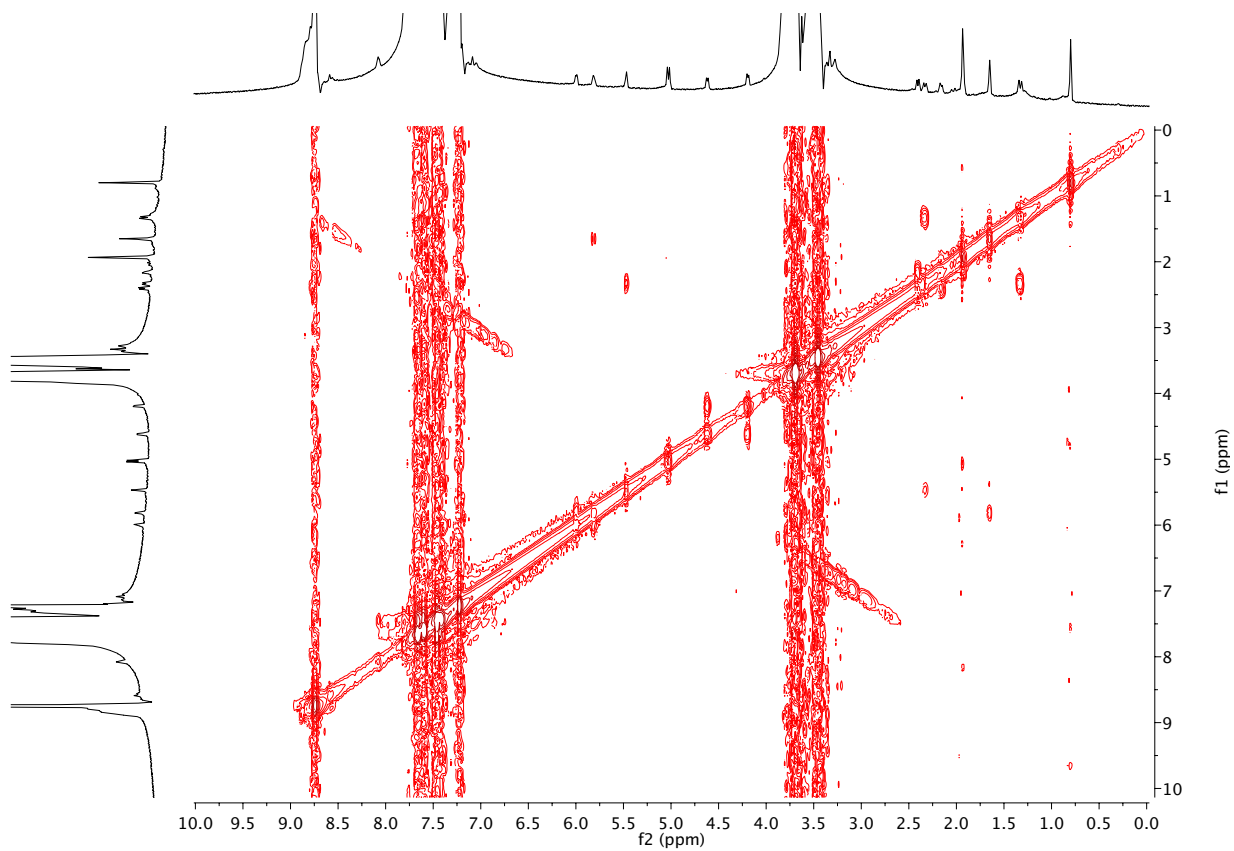


Figure S71. COSY Spectrum of (*S*)-MTPA Ester of **1** (**1a**) in Pyridine-*d*₅

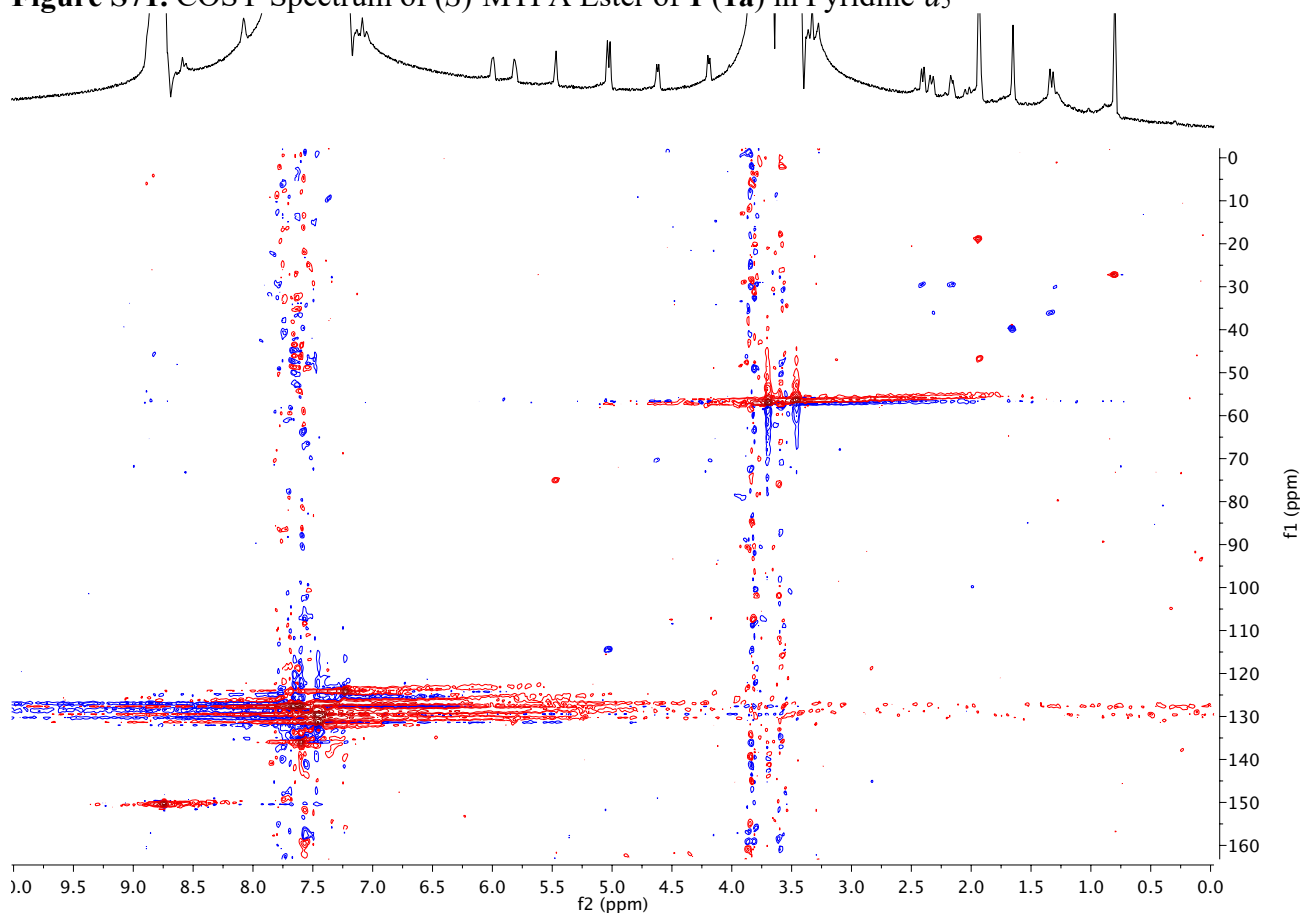


Figure S72. HSQC Spectrum of (*S*)-MTPA Ester of **1** (**1a**) in Pyridine-*d*₅

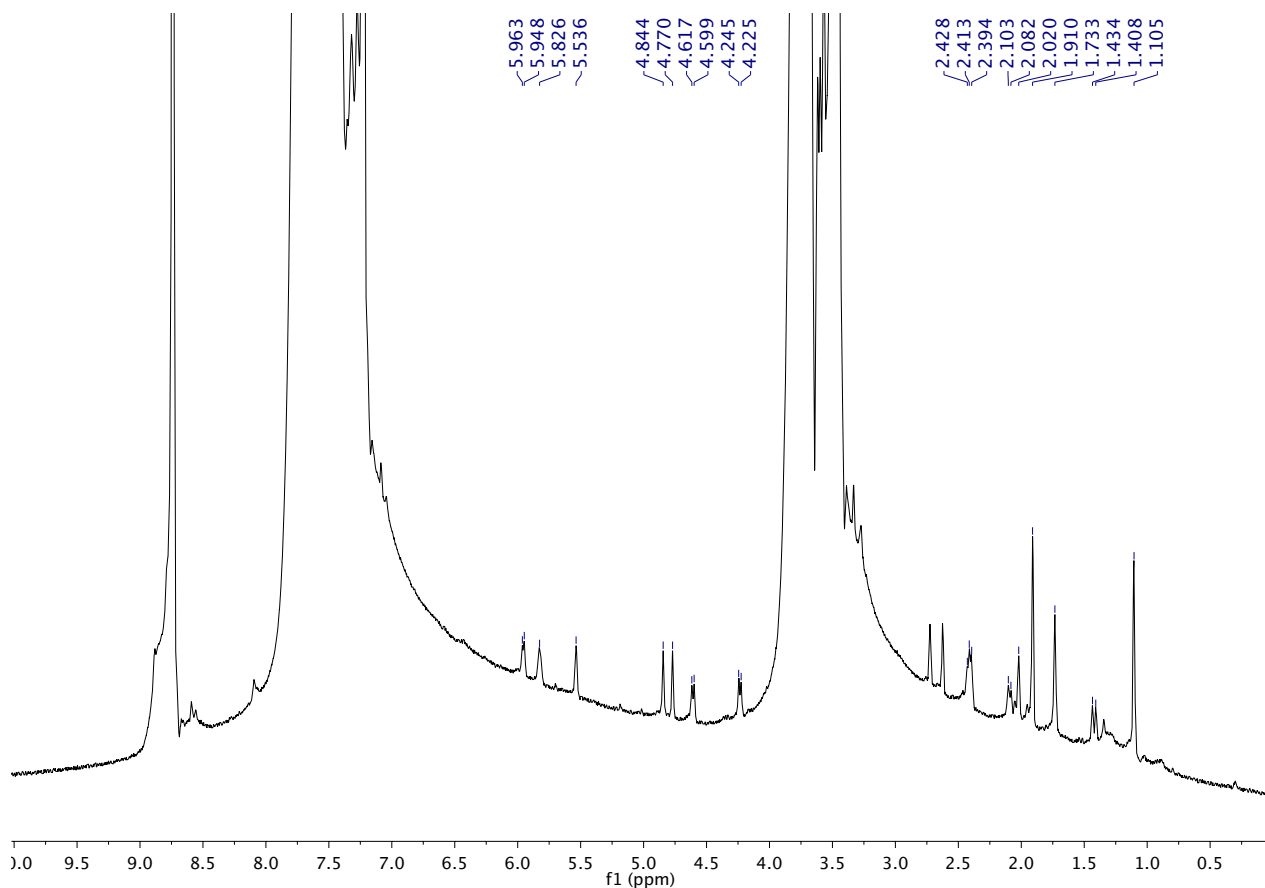


Figure S73. ^1H Spectrum of (*R*)-MTPA Ester of **1** (**1b**) in Pyridine- d_5

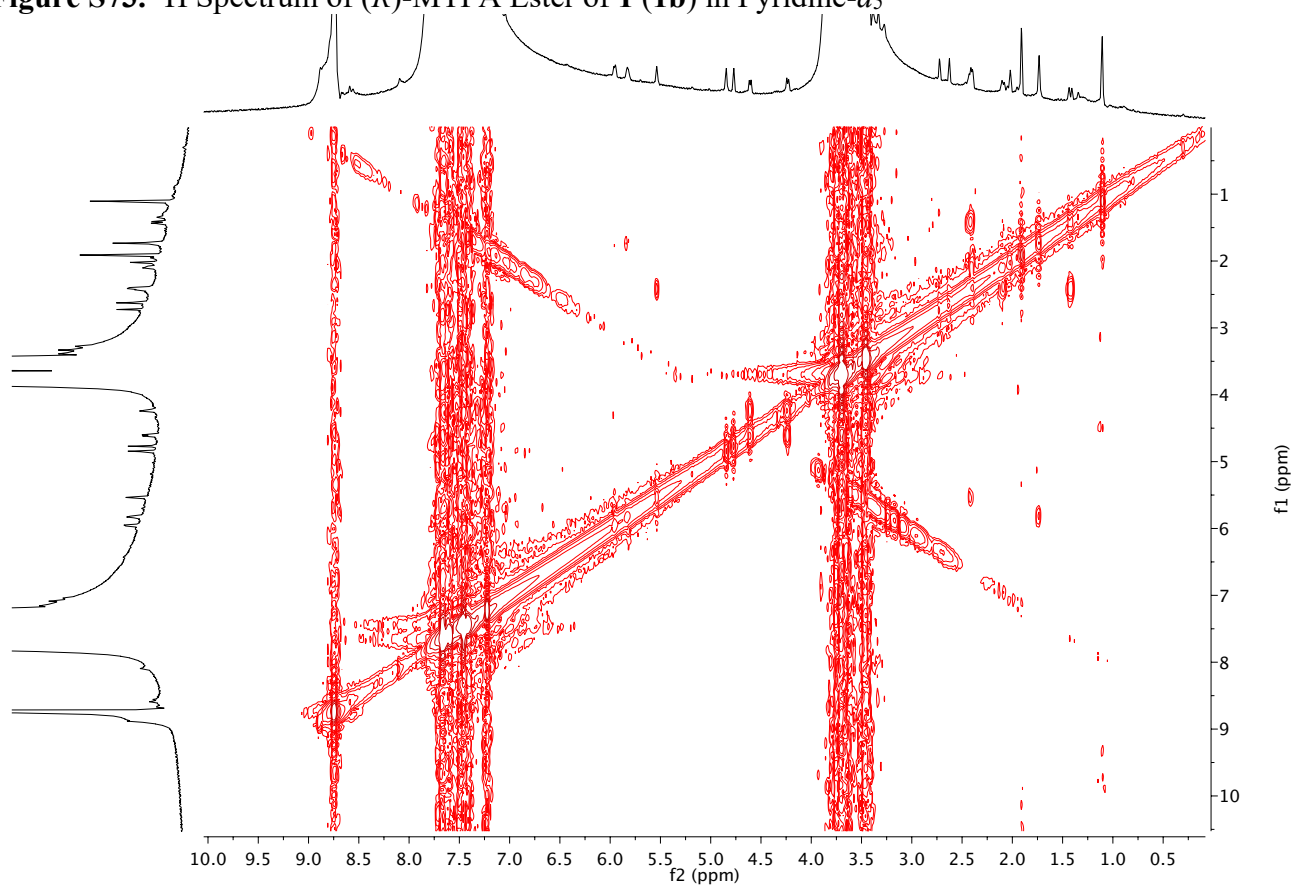


Figure S74. COSY Spectrum of (*R*)-MTPA Ester of **1** (**1b**) in Pyridine- d_5

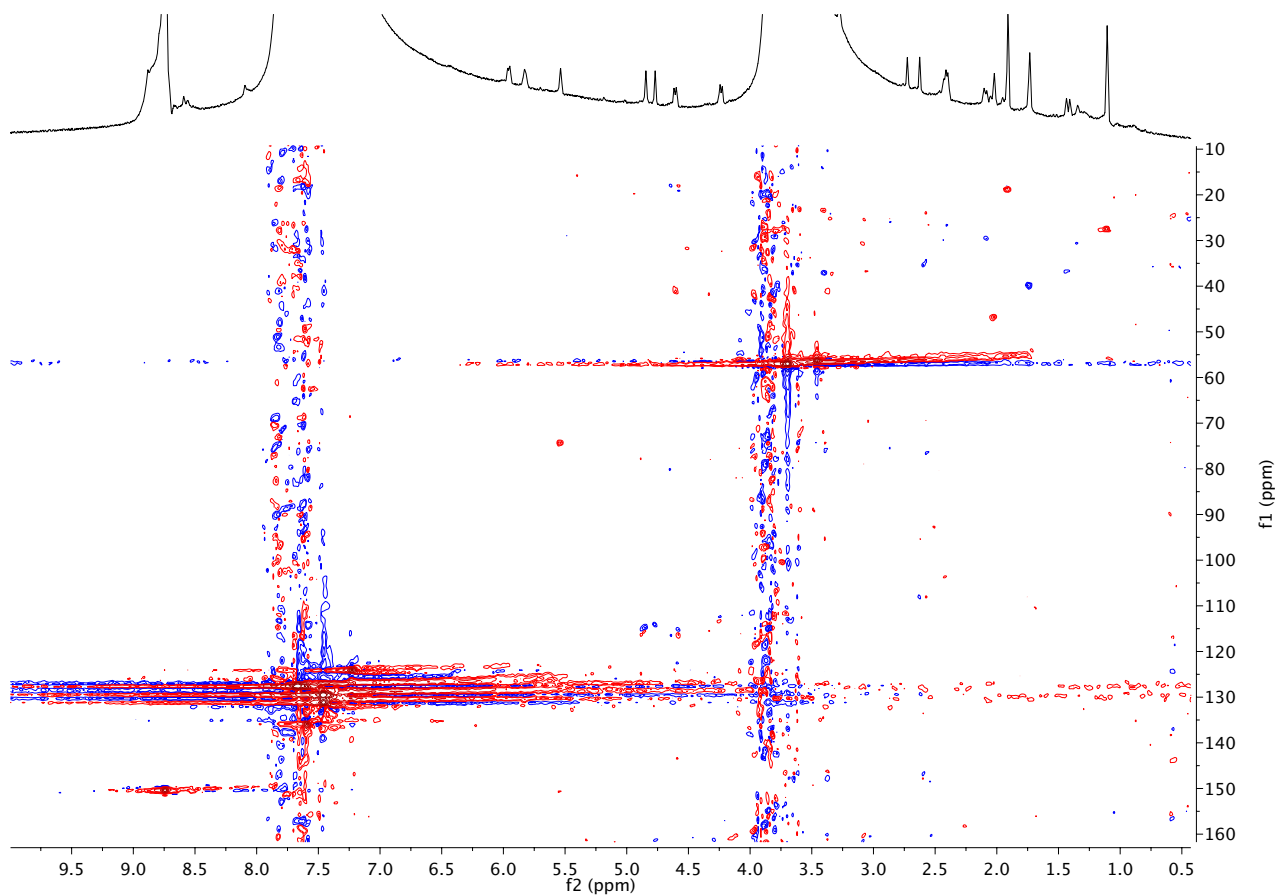


Figure S75. HSQC Spectrum of (*R*)-MTPA Ester of **1** (**1b**) in Pyridine-*d*₅

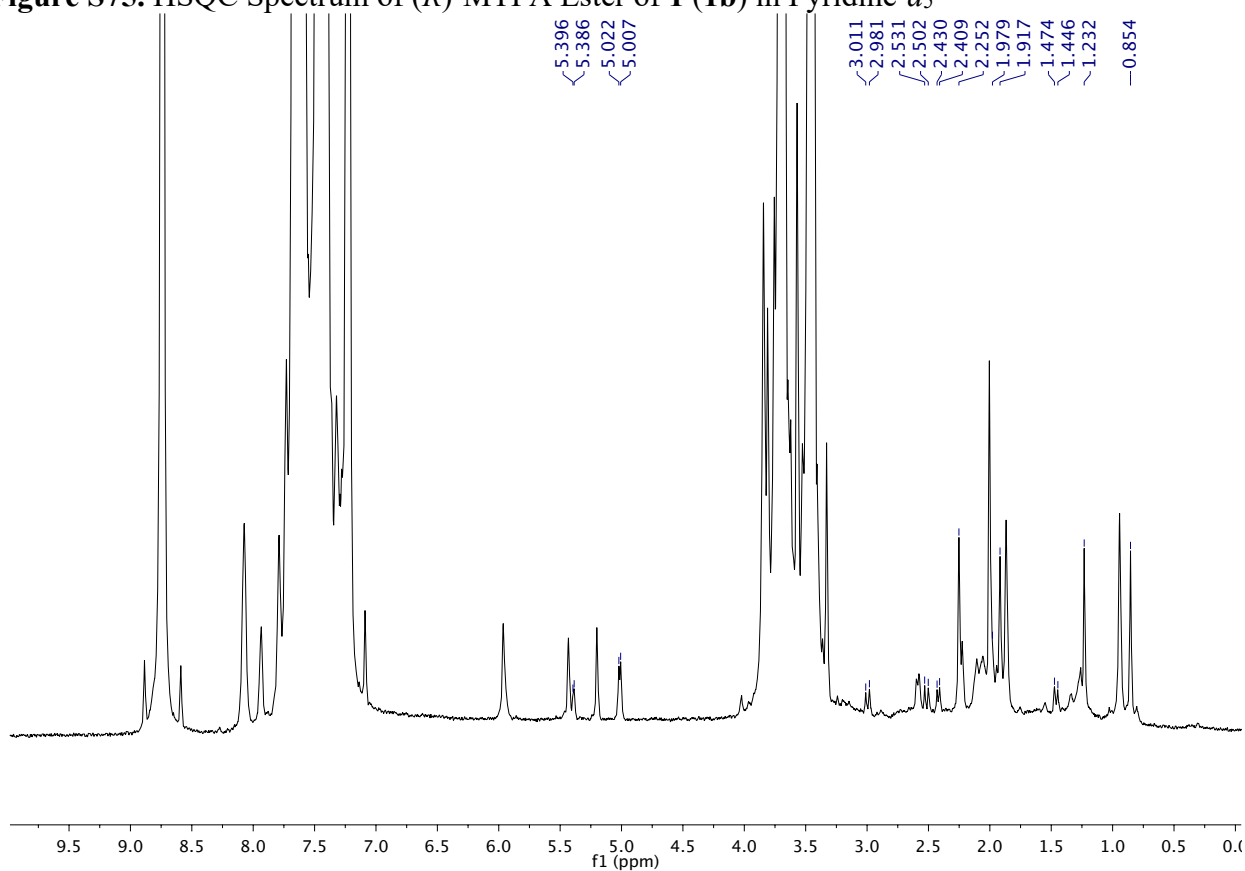


Figure S76. ¹H Spectrum of (*S*)-MTPA Ester of **2** (**2a**) in Pyridine-*d*₅

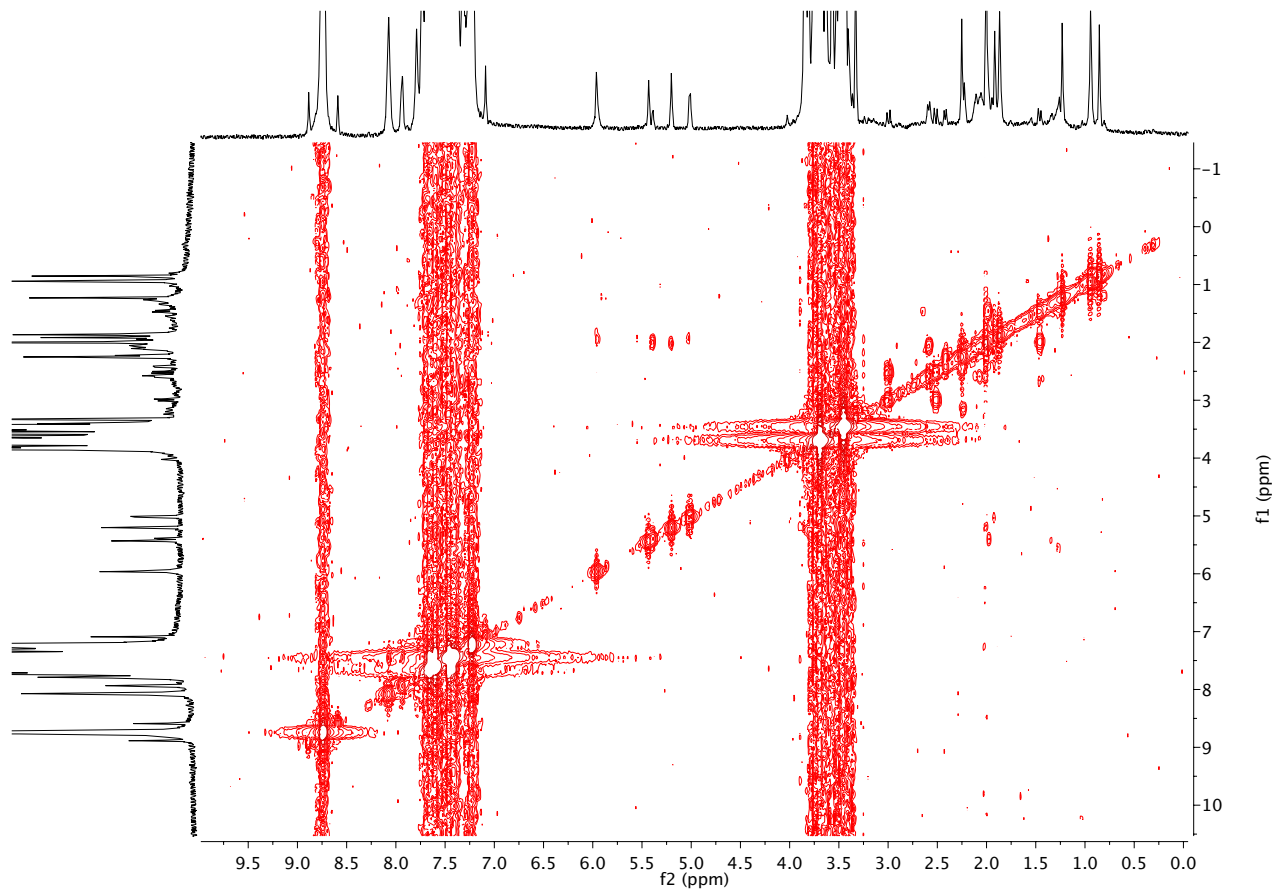


Figure S77. COSY Spectrum of (*S*)-MTPA Ester of **2** (**2a**) in Pyridine-*d*₅

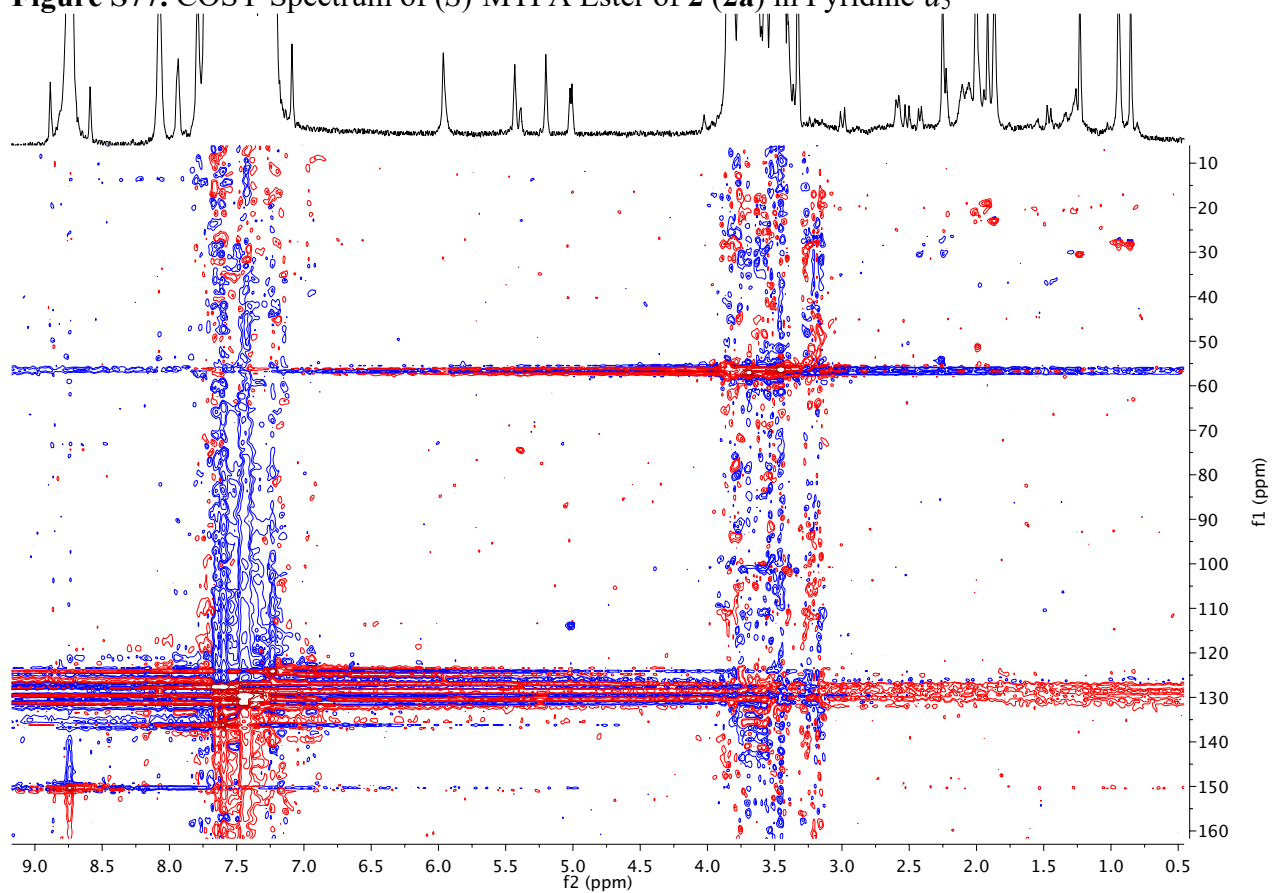


Figure S78. HSQC Spectrum of (*S*)-MTPA Ester of **2** (**2a**) in Pyridine-*d*₅

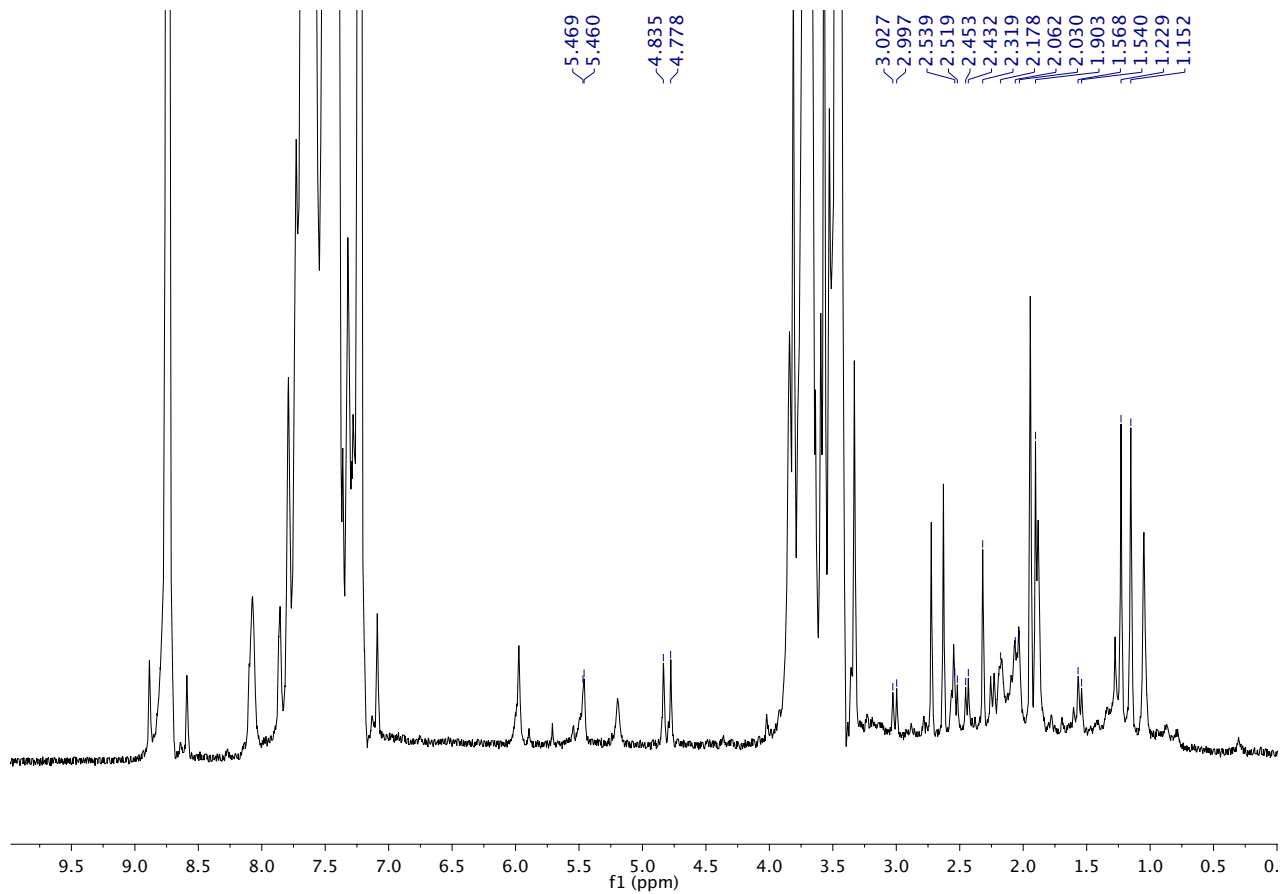


Figure S79. ^1H Spectrum of (*R*)-MTPA Ester of **2** (**2b**) in Pyridine- d_5

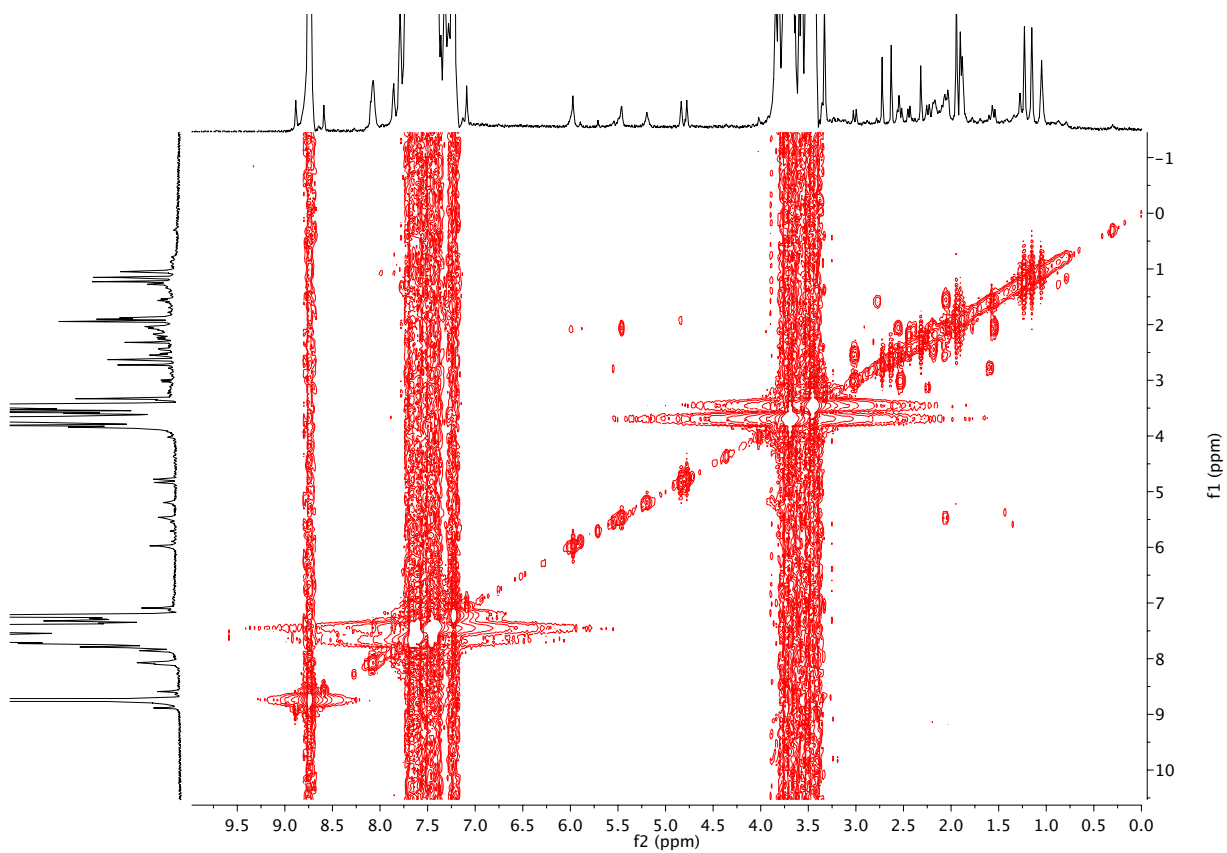


Figure S80. COSY Spectrum of (*R*)-MTPA Ester of **2** (**2b**) in Pyridine- d_5

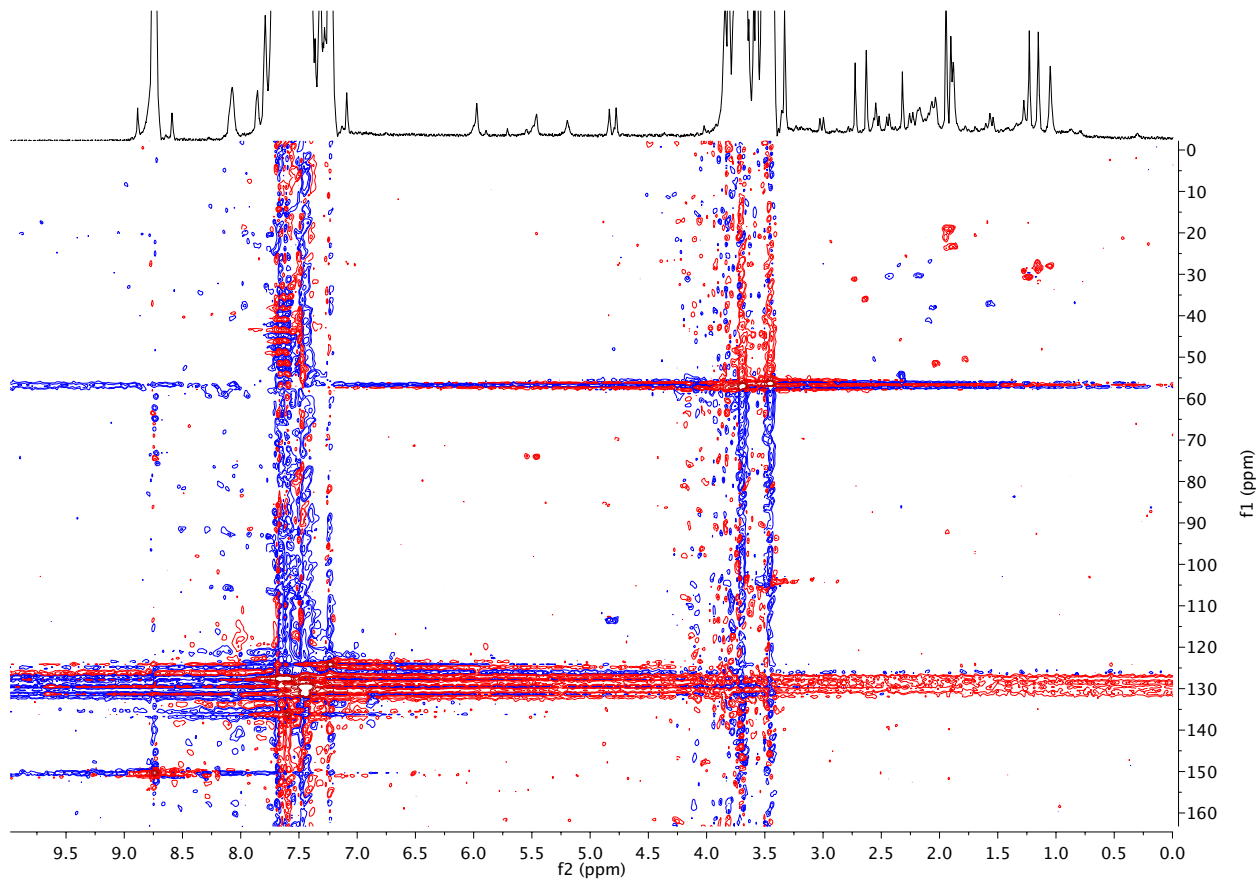


Figure S81. HSQC Spectrum of (*R*)-MTPA Ester of **2** (**2b**) in Pyridine-*d*₅

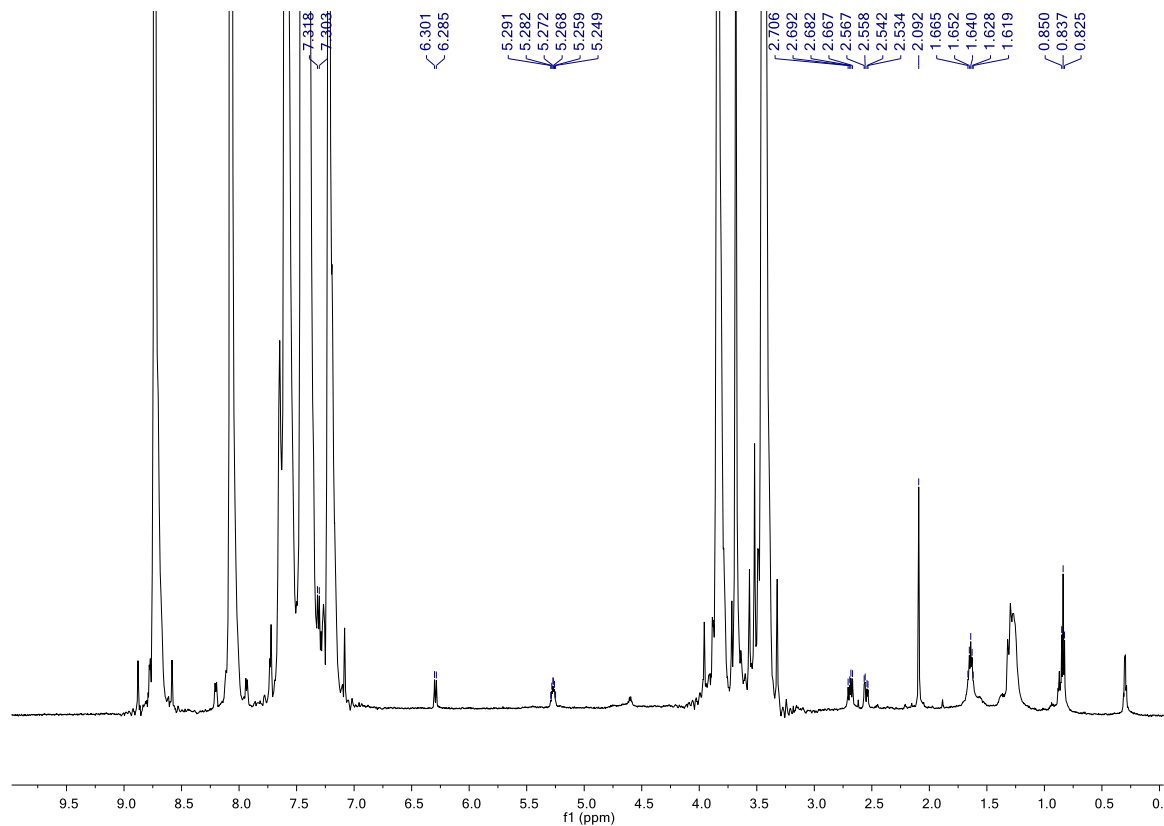


Figure S82. ¹H Spectrum of (*S*)-MTPA Ester of **11** (**11a**) in Pyridine-*d*₅

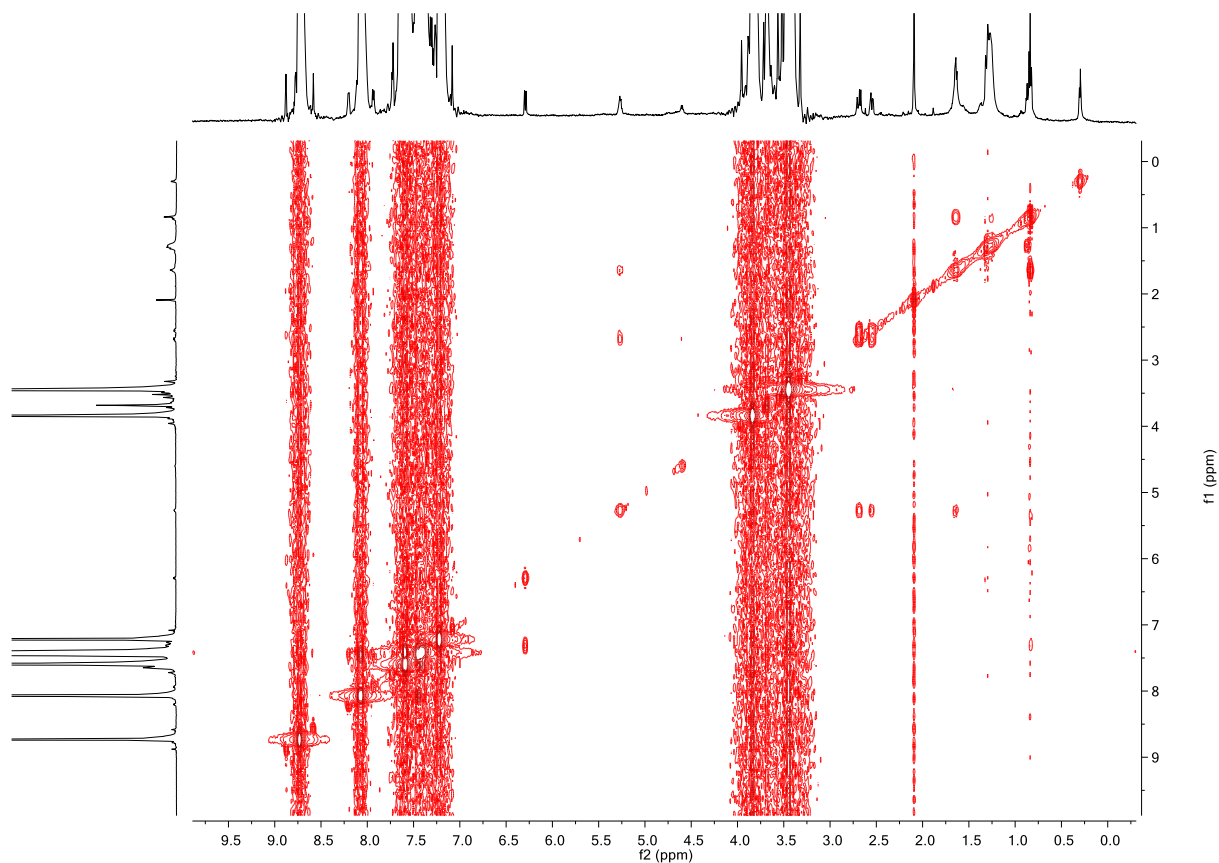


Figure S83. COSY Spectrum of (*S*)-MTPA Ester of **11** (**11a**) in Pyridine-*d*₅

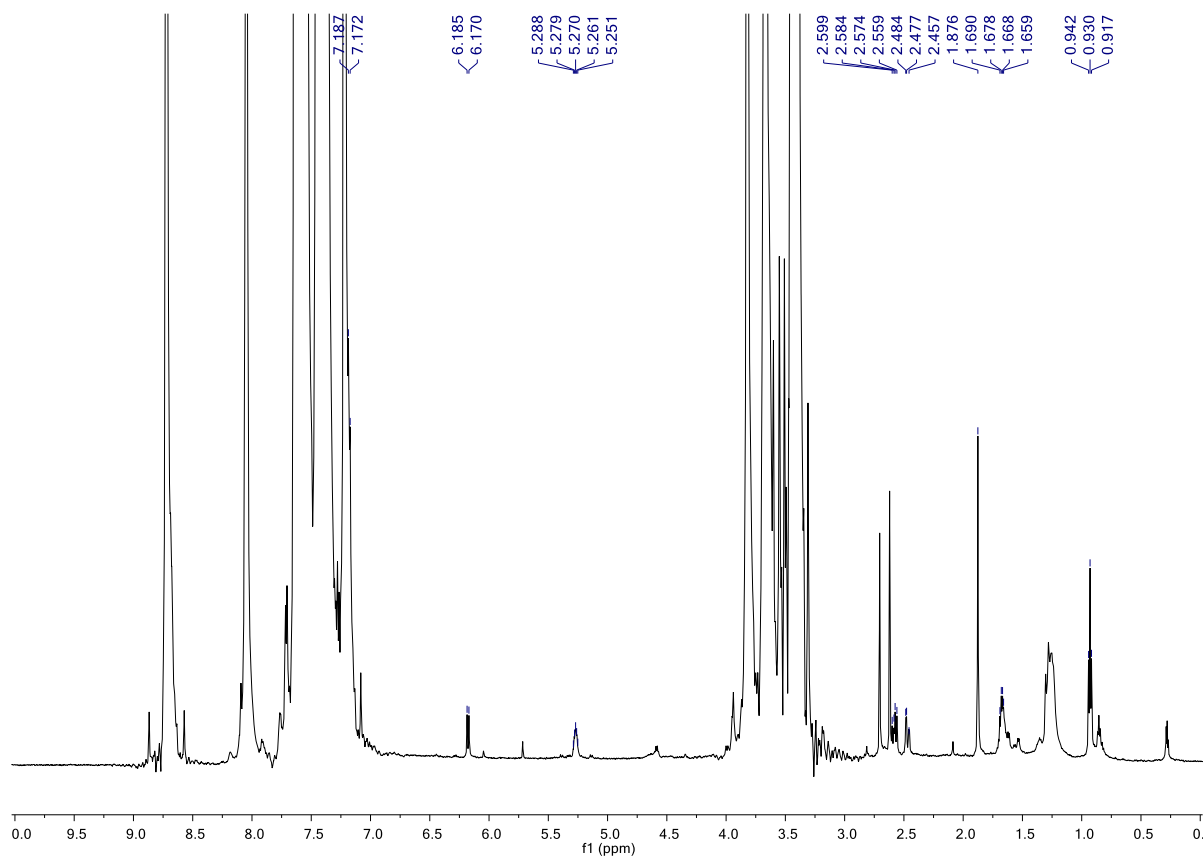


Figure S84. ¹H Spectrum of (*R*)-MTPA Ester of **11** (**11b**) in Pyridine-*d*₅

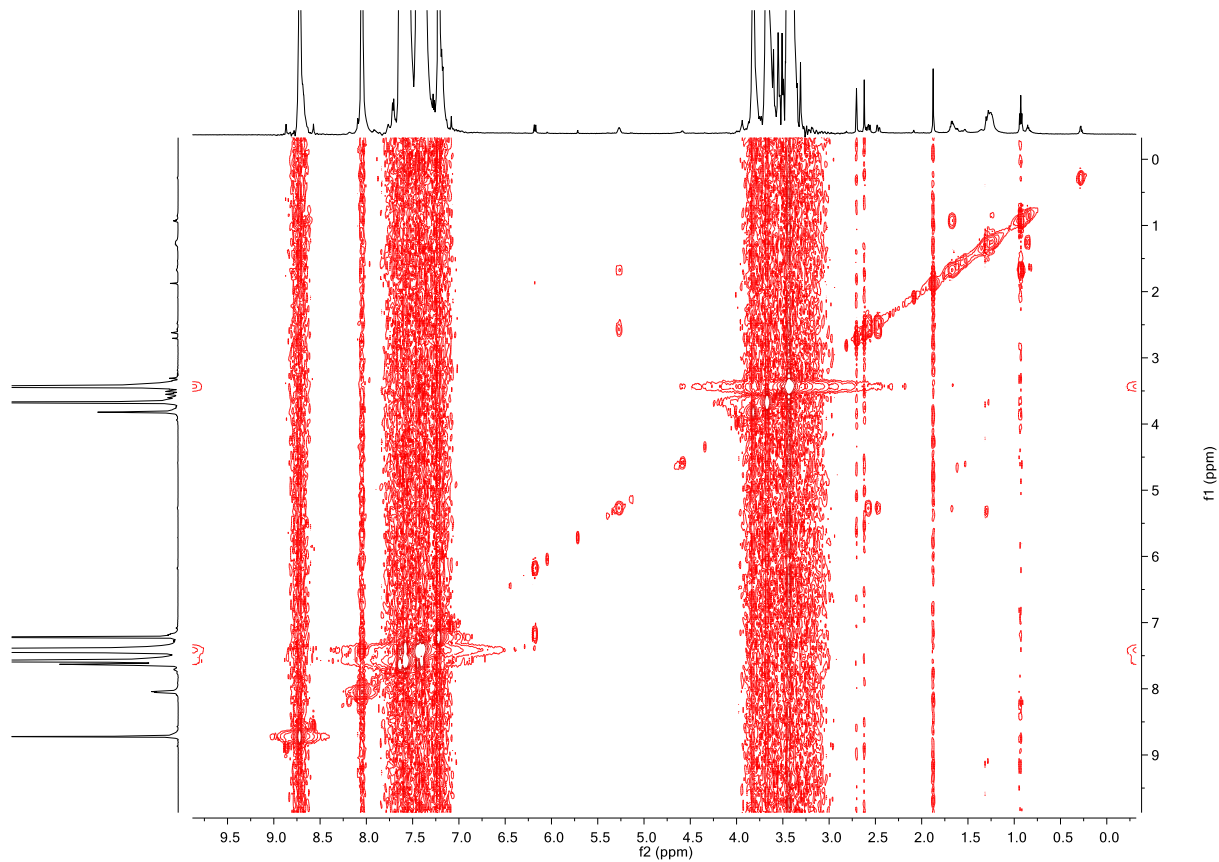


Figure S85. COSY Spectrum of (*R*)-MTPA Ester of **11** (**11b**) in Pyridine-*d*₅

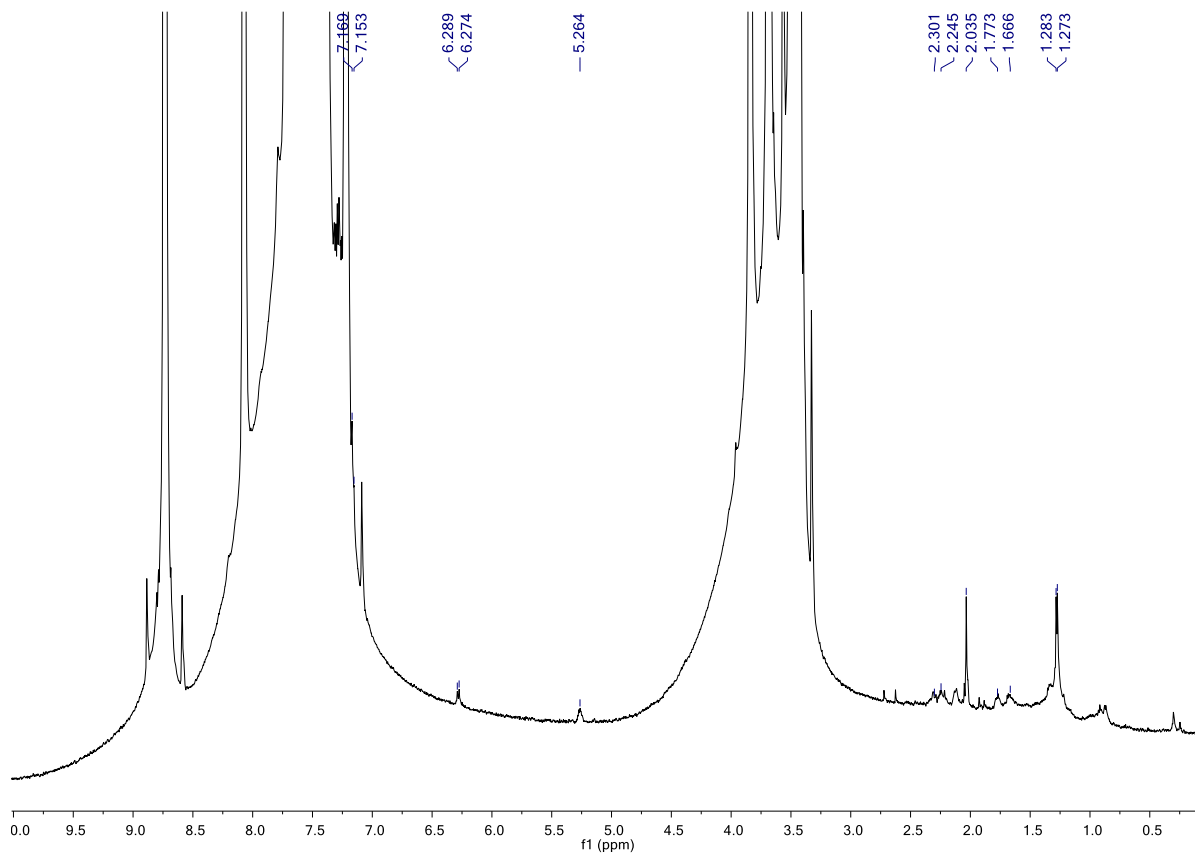


Figure S86. ¹H Spectrum of (*S*)-MTPA Ester of **12** (**12a**) in Pyridine-*d*₅

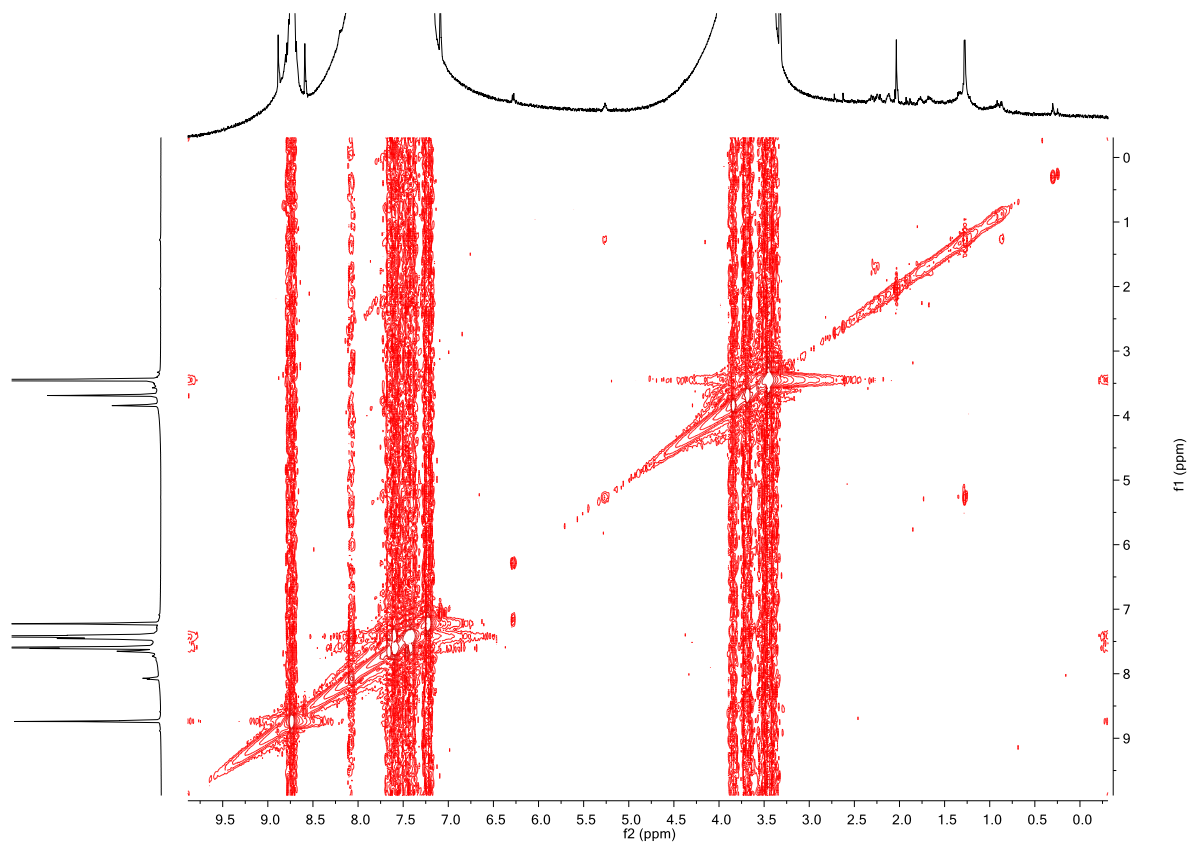


Figure S87. COSY Spectrum of (*S*)-MTPA Ester of **12** (**12a**) in Pyridine-*d*₅

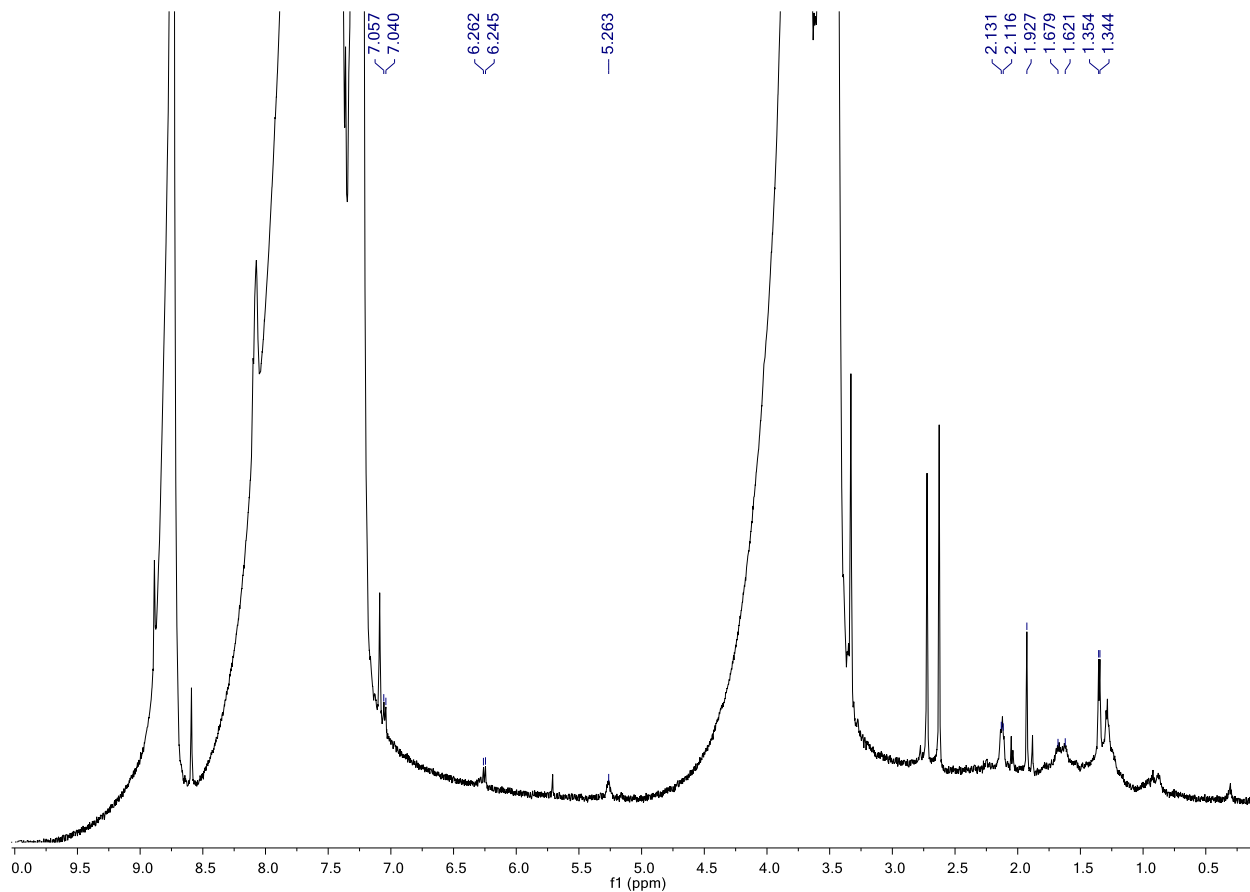


Figure S88. ¹H Spectrum of (*R*)-MTPA Ester of **12** (**12b**) in Pyridine-*d*₅

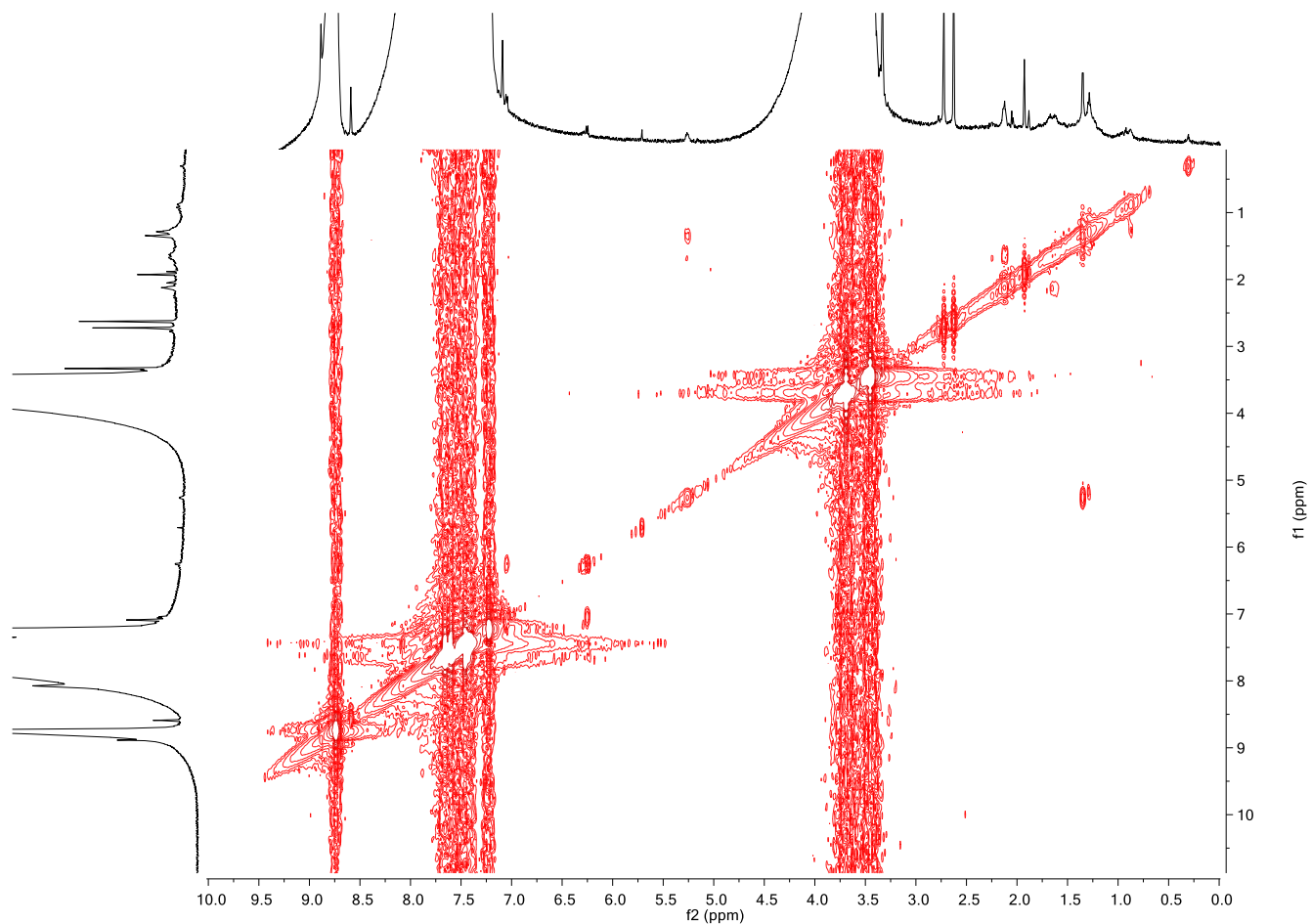


Figure S89. COSY Spectrum of (*R*)-MTPA Ester of **12** (**12b**) in Pyridine-*d*₅

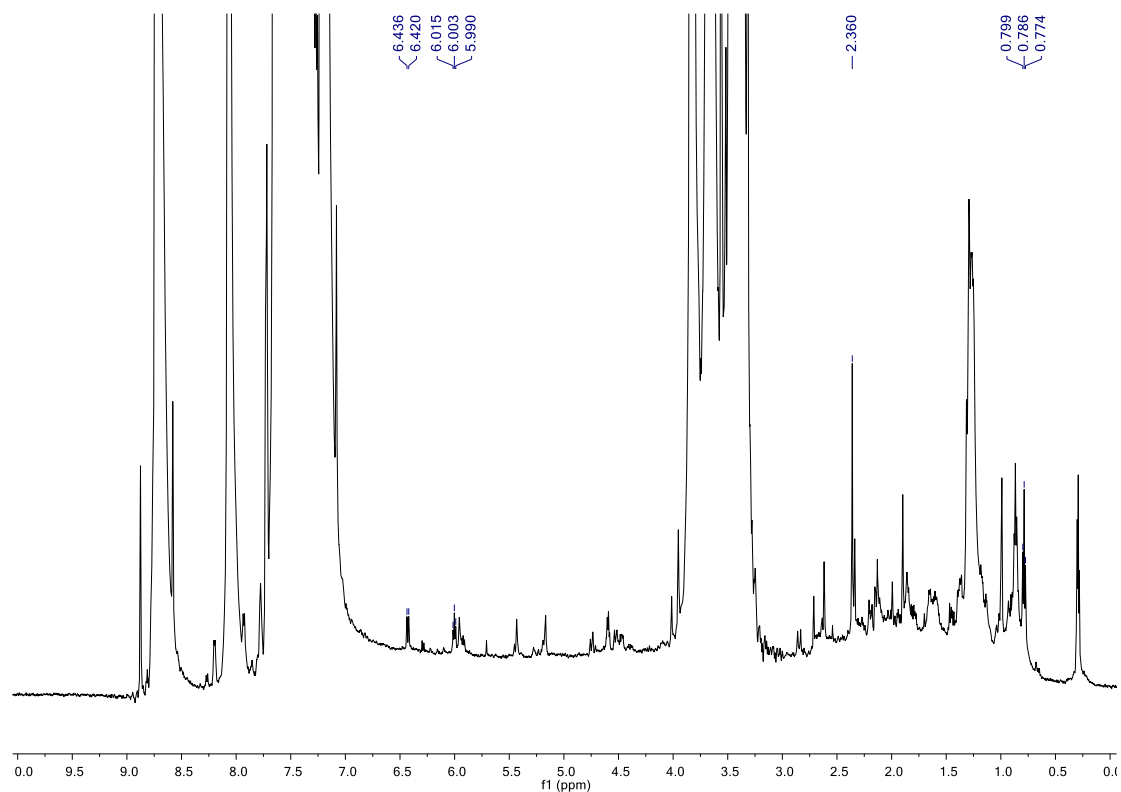


Figure S90. ¹H Spectrum of (*S*)-MTPA Ester of **13** (**13a**) in Pyridine-*d*₅

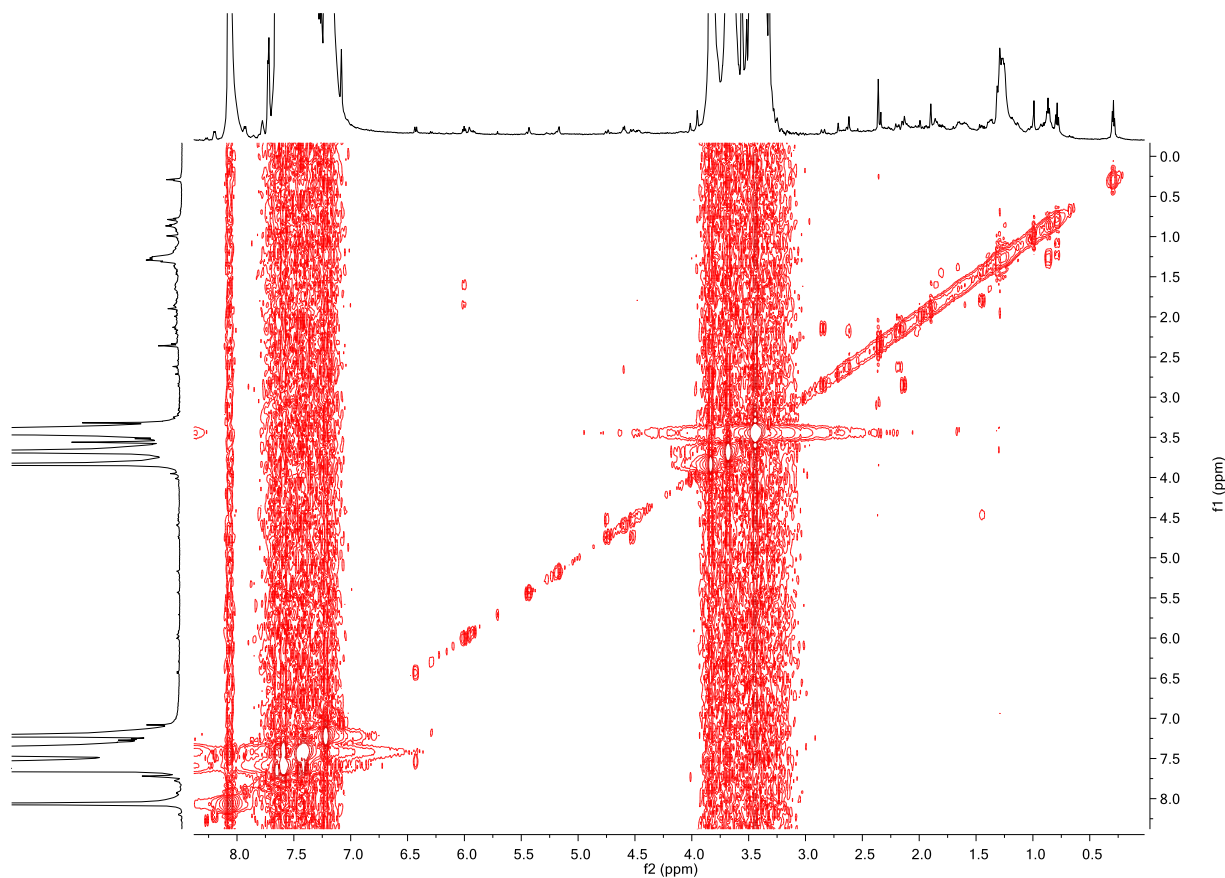


Figure S91. COSY Spectrum of (*S*)-MTPA Ester of **13** (**13a**) in Pyridine-*d*₅

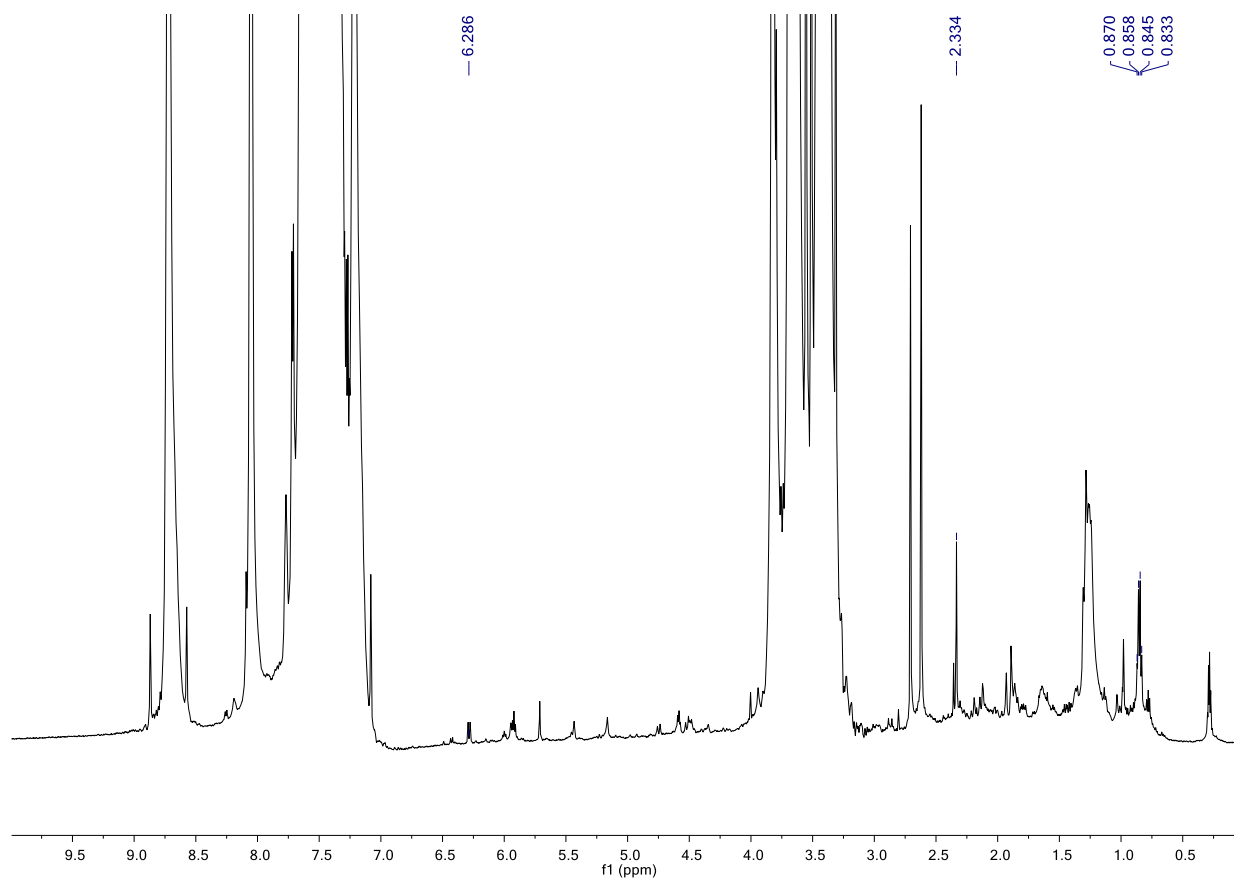


Figure S92. ¹H Spectrum of (*R*)-MTPA Ester of **13** (**13b**) in Pyridine-*d*₅

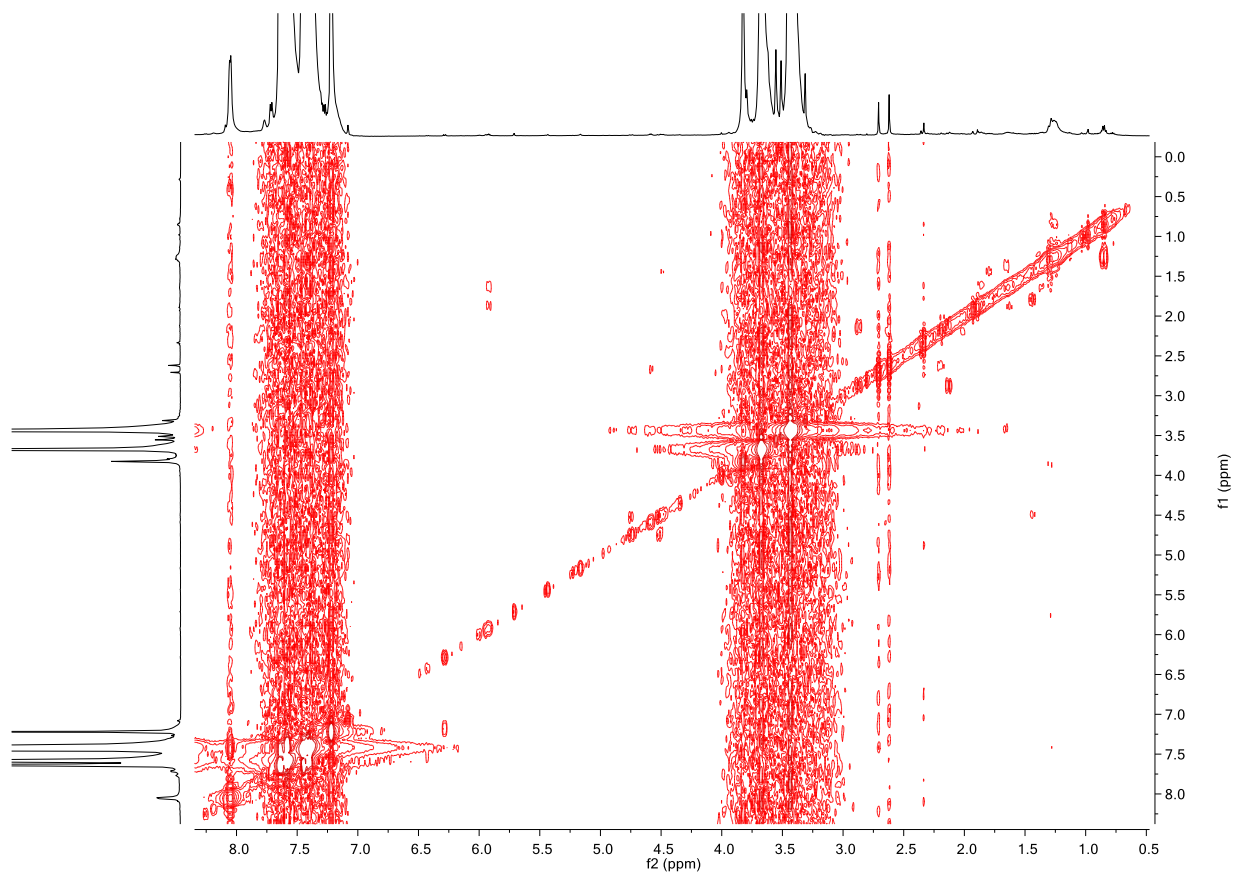


Figure S93. COSY Spectrum of (*R*)-MTPA Ester of **13** (**13b**) in Pyridine-*d*₅

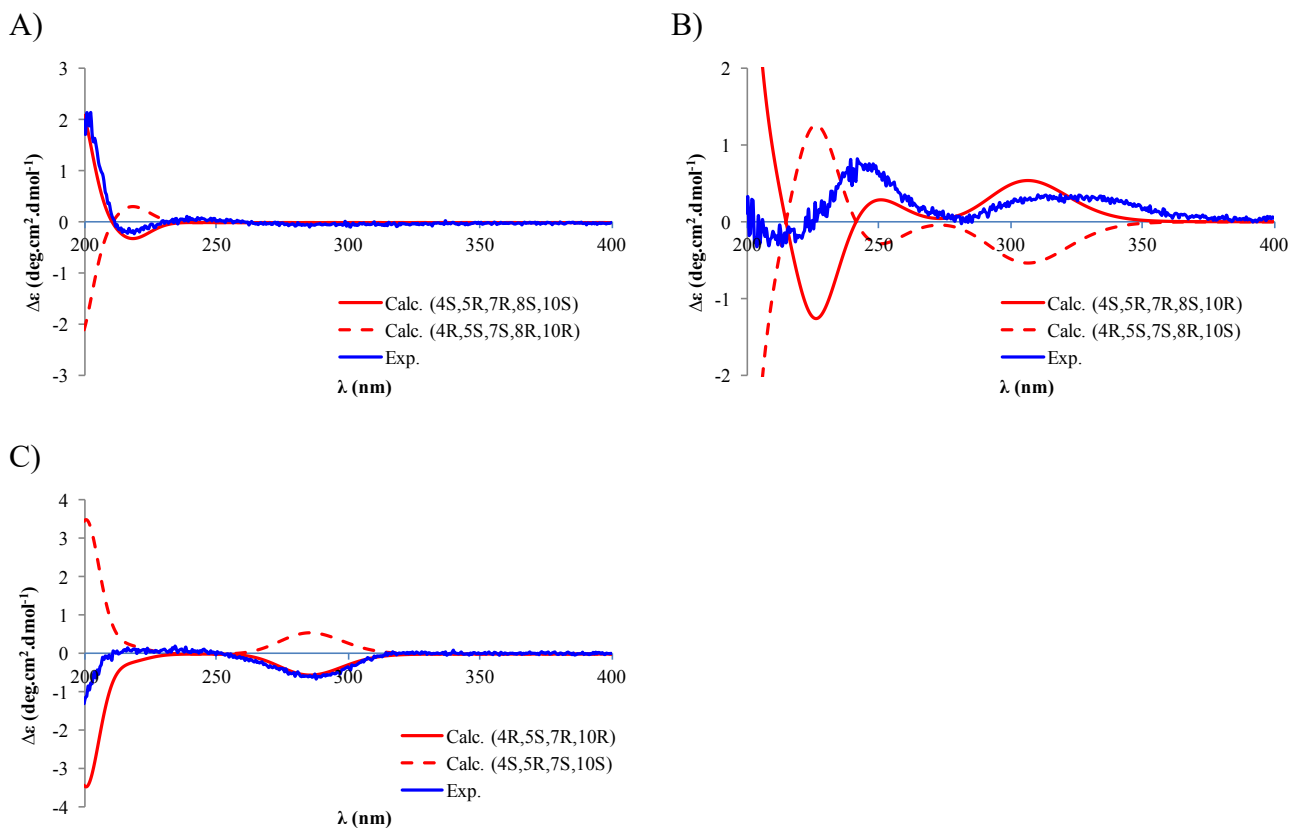


Figure S94. A) Experimental ECD spectrum of **1** and calculated ECD spectra of (4*S*, 5*R*, 7*R*, 8*S*, 10*S*)-**1** and (4*R*, 5*S*, 7*S*, 8*R*, 10*R*)-**1**; B) Experimental ECD spectrum of **2** and calculated ECD spectra of (4*S*, 5*R*, 7*R*, 8*S*, 10*R*)-**2** and (4*R*, 5*S*, 7*S*, 8*R*, 10*S*)-**2**; C) Experimental ECD spectrum of **3** and calculated ECD spectra of (4*R*, 5*S*, 7*R*, 10*R*)-**3** and (4*S*, 5*R*, 7*S*, 10*S*)-**3**;

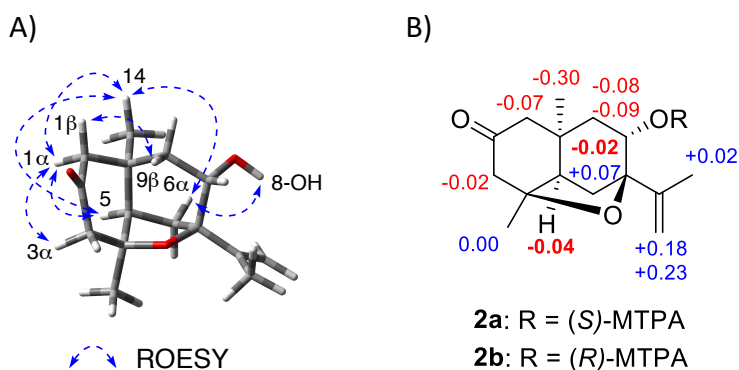


Figure S95. A: Key ROESY correlations of **2**. B: Mosher's ester analysis of MTPA-**2** (irregular $\Delta\delta^{SR}$ signs in bold).

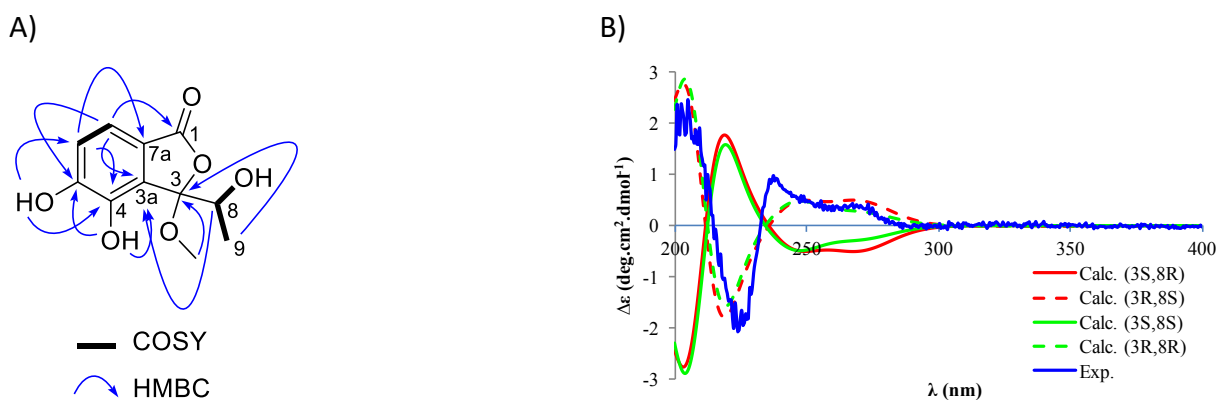


Figure S96. A: Key COSY and HMBC correlations for dictyophthalide A (**5**). B: The experimental ECD spectrum of **5** and calculated ECD spectra of (*3S*, *8R*)-**5**, (*3R*, *8S*)-**5**, (*3S*, *8S*)-**5** and (*3R*, *8R*)-**5**.

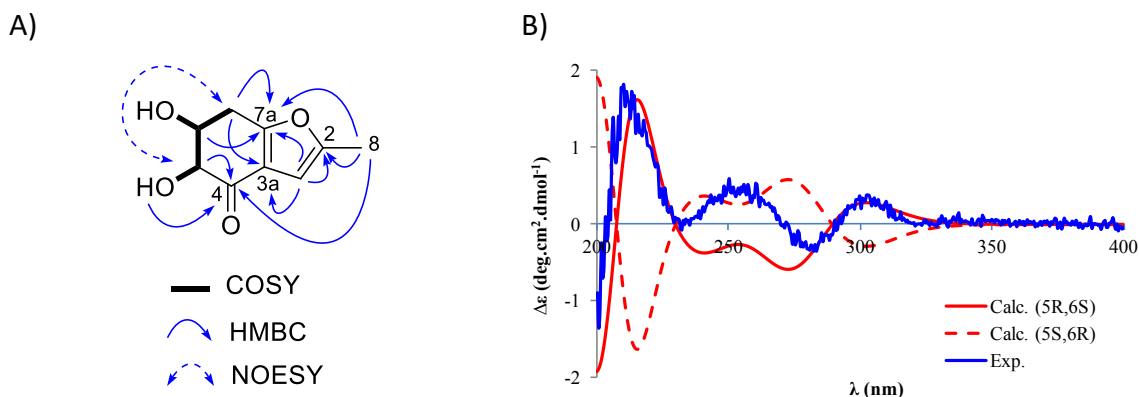


Figure S97. A: Key COSY, HMBC, and NOESY correlations for dictyofuran A (**6**). B: Comparison of the experimental (blue) and calculated (red) ECD spectra of **6**.

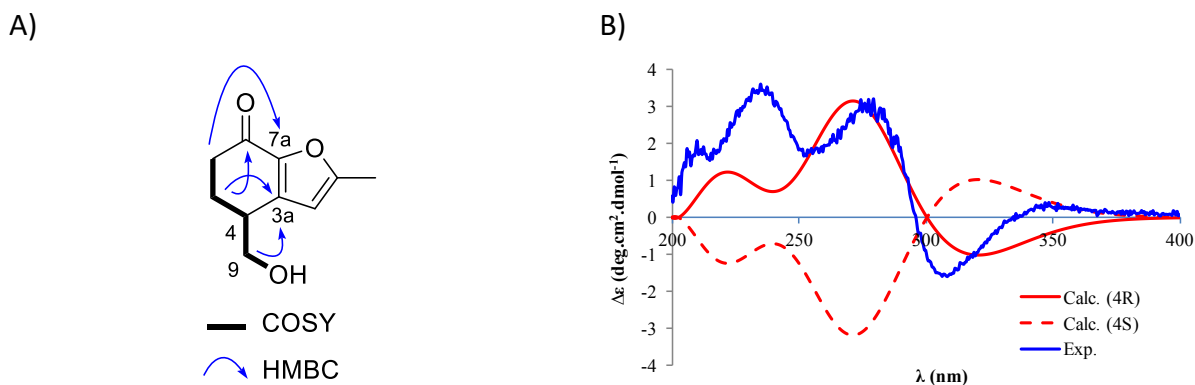


Figure S98. A: Key COSY and HMBC correlations of dictyofuran B (**7**). B: Comparison of the experimental (blue) and calculated (red) ECD spectra of **7**.

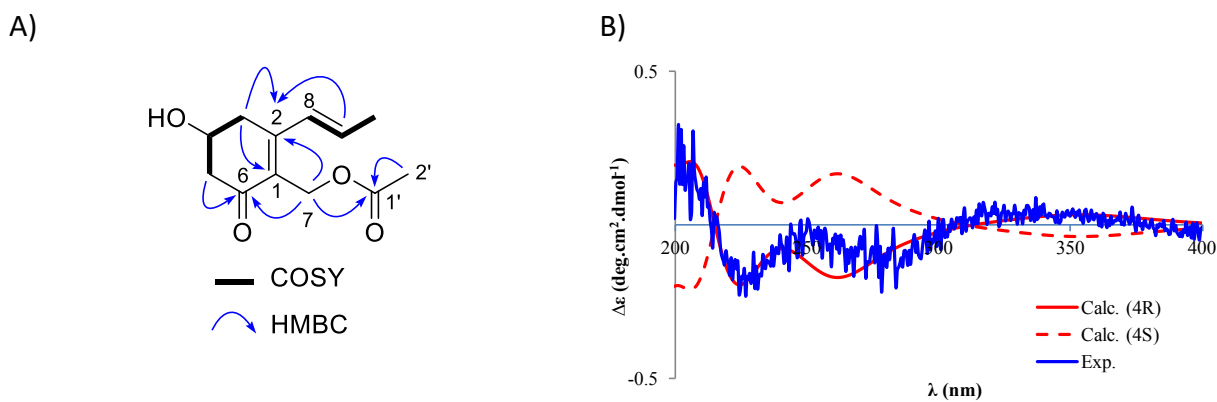


Figure S99. A: Key COSY and HMBC correlations for dictyosporone A (**10**). B: Comparison of the experimental (blue) and calculated (red) ECD spectra of **10**.

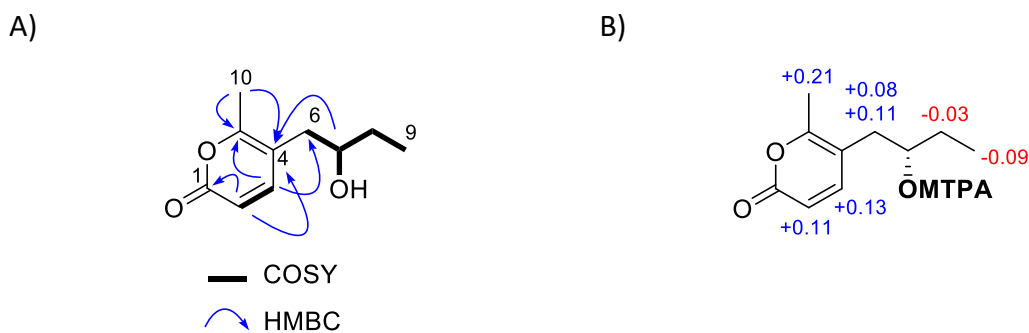
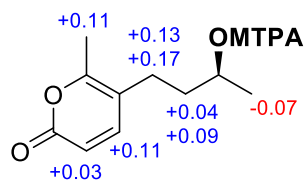


Figure S100. A: Key COSY and HMBC correlations of xylariolide E (**11**). B: $\Delta\delta^{S-R}$ values for the Mosher's ester derivatives of **11**.

A)



B)

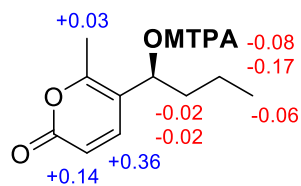


Figure S101. **A:** $\Delta\delta^{S-R}$ values for the Mosher's ester derivatives of xylariolide F (**12**). **B:** $\Delta\delta^{S-R}$ values for the Mosher's ester derivatives of **13**.